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RESEARCHES ON THE COMPLEX INORGANIC ACIDS.*

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I propose the term "complex inorganic acid" for a class of compounds which may be considered as formed by the union of two or more acids with elimination of water in such a manner as to form a whole which in its chemical relations behaves like an acid containing a single radical. Compounds of this character were observed at an early period in the history of chemistry, but their real nature was for a long time entirely unknown, and our positive knowledge of the subject dates from the discovery of the silico-tungstates by Marignac in 1861.† Berzelius had long before described and analyzed a compound which we should now write

$$3SiO_2 . 2V_2O_5 . 2P_2O_5 . 6H_2O,$$

the chemical relations of which are still to be studied.‡ He had also noticed the formation of peculiar yellow compounds when phosphoric or arsenic acids are digested with molybdic

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† Ann. de Chimie et de Physique, (4,) 3, 55.

‡ Lehrbuch der Chemie, 3, 1058.

teroxide.* These were again noticed and partially studied by Svanberg and Struve,† who employed a solution of ammonic molybdate as a test for the presence of phosphoric acid. Sonnenschein‡ appears to have first shown that phosphoric oxide was an essential constituent of the yellow compound formed. Finally Debray assigned to the ammonium salt the formula

$$20MoO_3 . P_2O_5 . 3(MH_4)_2O + 3H_2O,$$

and separated the corresponding acid.

In a paper presented to the Association of German Naturalists and Physicians in August, 1872,§ Scheibler described salts of two different phosphotungstic acids, and gave formulas for the acids themselves, as well as for a sodium salt belonging to a third series, all of which, however, he regarded as provisional. Since then nothing further has appeared upon the subject from Scheibler's pen, and I have consequently felt at liberty to include the phosphotungstates in my own work.

My investigation of the complex inorganic acids had advanced but little before I found it necessary to study the alkaline salts of tungstic acid with special care. This study has alone occupied a great deal of time, and has proved one of extraordinary difficulty, in spite of the previous labors of Laurent, Lotz, Scheibler, Zettnow, Marignac, and others. The difficulties in question are mainly these:—

1. The alkaline tungstates are numerous and unusually complex. Salts of essentially different formulas approach so closely in percentage composition, that the differences lie very near the unavoidable errors of analysis. Thus Scheibler maintains that the formula of a particular sodium salt is

$$7WO_3 . 3Na_2O + 16aq.$$

while, according to Marignac, the same salt must be represented by

$$12WO_3 . 5Na_2O + 28aq.$$

The analyses are hardly sufficiently close to decide the question upon purely analytical grounds.

* Lehrbuch, 3, 1044.
† K. Sv. Vet. Handlingar, 1848, p. 1.
‡ Journal für prakt. Chemie, 53, 342.
§ Berichte der deutschen chem. Gesell. 5, 801.

2. Almost all the alkaline tungstates are efflorescent in a very marked degree.

3. The salts of one series agree so closely in chemical properties with those of the next, that distinctive tests are wanting, and analysis does not always suffice to distinguish two salts even when unmixed. Mixtures are naturally very hard to deal with.

4. Monoclinic and triclinic forms predominate very largely, but owing to rapid efflorescence it is very difficult to make good measurements of crystals. The resemblance between the forms of different compounds is frequently very close.

5. Many salts are decomposed by boiling, or even by hot water, yielding two or more different salts in solution. These usually recombine in the act of crystallization or on cooling the solution, but the reactions of hot and cold solutions are often, as I shall show, very different.

In determining the tungstic oxide in these compounds, I have employed the method of Berzelius with mercurous nitrate almost exclusively, but I have modified the process slightly so as to gain materially in accuracy. To the hot solution of the tungstate mercurous nitrate is added until in small excess. Mercuric oxide, prepared by precipitating the chloride by sodic hydrate, is then added until the yellow mercurous tungstate takes a reddish hue which is persistent after boiling. If the solution is boiled before filtering it clears rapidly, and the precipitate becomes rather more compact. The filtration and washing are then very easy and expeditious. The precipitate must be ignited as long as it loses weight. By this process Dr. Gooch, my assistant, obtained results which in two successive analyses of the same preparation rarely differed by 0.1 p. ct. The water determinations were always made by simple ignition. They almost invariably agree within a few hundredths. In the greater number of cases the alkaline base was determined from the loss, as the results obtained in this manner are far more accurate than those yielded by the direct method. But in some doubtful salts the alkali was determined directly. Ammonia was always estimated by boiling the compound with an excess of sodic hydrate, collecting the ammonia in chlorhydric acid, and weighing it as chloride.

The only objection to the method of determining tungstic oxide above given is, that the precipitate of mercurous tungstate is rather voluminous, so that it is necessary to work with quantities of alkaline tungstate not much exceeding one gram in weight. I endeavored to overcome this difficulty by omitting the mercuric oxide and evaporating the solution and precipitate, after the addition of mercurous nitrate, to perfect dryness in a water bath, continuing the heat until all the free nitric acid was expelled. This method gave results which corresponded very closely with those obtained by the use of mercuric oxide to neutralize the free nitric acid, and in consequence of the extremely compact form of the dry mercurous tungstate, permitted the employment of much larger quantities of salt for analysis. On the other hand, it presents another difficulty, arising from the fact that the dry mercurous tungstate adheres with excessive tenacity to the evaporating vessels, whether of glass, porcelain, or platinum, so that the first method is on the whole to be preferred.

The separation of tungstic oxide from other bases is best effected by fusing the salt with an excess of potassio-sodic carbonate and dissolving out the alkaline tungstates formed.

Normal sodic tungstate has long been known, and all the analyses concur in assigning to it the formula

$$WO_4Na_2 + 2aq.$$

It is now to be had from various German firms in a state of purity, and forms the most convenient material for the study of the compounds of tungsten. The acid salt analyzed by Anthon, and to which the formula

$$W_2O_7Na_2 + 4aq.$$

was long ascribed, is now well known to have an entirely different composition; but Lefort* has recently endeavored to show that ditungstates and tritungstates really exist, and has described a number of salts of each series. Lefort obtains sodic ditungstate by adding glacial acetic acid to a saturated solution of the neutral salt until the reaction with litmus becomes acid. After a day or two the salt separates in long prismatic crystals, with the formula

$$W_2O_7Na_2 + 6aq.$$

* Ann. de Chimie et de Physique. (5,) 9, 93.

I have repeatedly attempted to prepare the ditungstate by this process, but without success in any one instance, the resulting salts being, as I shall show further on, in all cases very different in composition. Lefort prepared sodic tritungstate by pouring a concentrated solution of the ditungstate into a boiling solution of glacial acetic acid. His analyses agree fairly well with his formulas, and I have adopted his results without question, in the belief that my own inability to reproduce them was due to the omission in his paper of some matter of detail which appeared insignificant, but which was really important.

Ten to Four Sodium Salt.—The salt to which I have given this name appears to have been first observed by Forcher,* who obtained it by passing a current of carbonic dioxide for some days through a solution of the normal tungstate. Forcher gives the formula

$$5WO_3 . 2Na_2O + 12H_2O,$$

and suggests, though without adducing any evidence in support of his view, that it may be a double salt, with the formula

$$3WO_3 . Na_2O + 2WO_3 . Na_2O.$$

Marignac, who appears to have been unacquainted with Forcher's paper, soon afterward described the same salt as an accidental product, attributing to it the formula

$$5WO_3 . 2Na_2O + 11H_2O.$$

Finally, Lefort† obtained it by the action of acetic acid upon a solution of the normal tungstate, and, without citing the results of Forcher, also proposed the formula

$$5WO_3 . 2Na_2O + 11H_2O.$$

I have obtained the salt by the following process, which appears to be the most convenient. Normal sodic tungstate,

$$WO_3 . Na_2O + 2aq.$$

is to be dissolved in water, and acetic acid added, in small portions at a time, to the boiling solution, until the reaction becomes strongly acid. Alcohol then precipitates the 10 : 4 tungstate as a heavy oil, which soon becomes a solid mass.

* Wiener Akad. Berichte, 44, 2, 177. † Loc. cit.

The solution on standing some days deposits colorless crystals, which are usually much twinned, and, according to Marignac, belong to the monoclinic system. They effloresce readily in dry air and are soluble, according to Forcher's determination, in 12.6 parts of water at 22° C. When heated they fuse to a yellow liquid, which on cooling gives a white crystalline mass nearly insoluble in cold water but dissolved by long boiling. I assign to the crystallized hydrate the formula

$$10WO_3 . 4Na_2O + 23H_2O, \text{ or } 10WO_3 . 4Na_2O . 2H_2O + 21aq.$$

with which all the analyses agree very closely. Of the salt,

I. { 1.4152 gr. lost 0.1963 gr. by ignition = 13.88 p. ct.
{ 0.4095 gr. gave 0.3194 gr. WO_3 = 77.99 "

II. { 1.1182 gr. lost on ignition 0.1558 gr. water = 13.94 "
{ 0.8950 gr. gave 0.6968 gr. WO_3 = 77.85 "

III. { 1.3594 gr. lost on ignition 0.1862 gr. water = 13.70 "
{ 0.5340 gr. gave 0.4155 gr. WO_3 = 77.80 "

IV. { 1.1660 gr. lost on ignition 0.1624 gr. water = 13.93 "
{ 0.5981 gr. gave 0.4659 gr. WO_3 = 77.89 "

V. { 1.3594 gr. lost on ignition 0.1862 gr. water = 13.70 "
{ 0.5340 gr. gave 0.4155 gr. WO_3 = 77.80 "

The formula $10WO_3 . 4Na_2O + 23aq.$ requires

		Calc'd.	1.	2.	3.	4.	5.	Forcher.	Marignac.
$10WO_3$	2320	77.80	77.99	77.85	77.80	77.89	77.80	77.82	77.88
$4Na_2O$	248	8.32	8.13	8.21	8.50	8.18	8.50	8.16	8.39
$23H_2O$	414	13.88	13.88	13.94	13.70	13.93	13.70	13.88	13.53
	2982	100.00						99.86	99.80

The means of all these analyses may be compared with the three formulas above given.

	WO_3	Na_2O	H_2O
For the ratio 10 . 4 . 22	78.27	8.37	15.36
" " 10 . 4 . 24	77.63	8.16	14.21
" " 10 . 4 . 23	77.80	8.32	13.88
Means of new analyses,	77.86	8.30	13.83

The analyses therefore leave no reasonable doubt as to the true constitution of the salt. The solution of the 10 : 4 sodic

tungstate has a distinct acid reaction, but it is very difficult to determine the limits of the basicity in this series, because no salts could be obtained having a number of molecules of fixed base higher than four. On the other hand, the white insoluble mass obtained by igniting the crystalline hydrate must have the formula

$$10WO_3 . 4Na_2O,$$

and I consider it a true pyro-salt. When boiled for some time with water, the pyro-salt dissolves and the original salt crystallizes from the solution. The case appears to be exactly analogous to that of sodic metatungstate, the insoluble

$$4WO_3 . Na_2O$$

of Scheibler and Marignac, giving the normal sodic metatungstate,

$$4WO_3 . Na_2O + 10aq.$$

when heated with water in a sealed tube. The reactions of the 10 : 4 salt with metallic solutions are extremely similar to those of the 12 : 5 salt,

$$12WO_3 . 5Na_2O + 28aq.$$

so that in fact it is difficult to distinguish between the two in any other way than by the habitus of the crystals and by analysis.

When the 10 : 4 salt is dissolved in water and a current of sulphydric acid gas passed into the solution to the point of saturation, the liquid becomes at first yellow, and finally orange red. On standing or evaporation, it deposits brown tungstic sulphide, WS_3, and the still faintly yellow mother liquor gives fine colorless triclinic crystals, which are separate and distinct, not twinned or aggregated in masses like the 10 : 4 salt. These crystals after recrystallization have the formula of the 12 : 5 salt presently to be described, namely,

$$12WO_3 . 5Na_2O + 28aq.$$

as the following analyses show:—

1.6491 gr. gave	1.2760 gr. WO_3	= 77.38 p. ct.
2.3696 gr. lost	0.3308 gr. water	= 13.96 "
2.0037 gr. "	0.2790 gr. "	= 13.92 "

		Calc'd.	Found.
$12WO_3$	2784	77.38	77.38
$5Na_2O$	330	8.61	8.68
$28H_2O$	504	14.01	13.92 13.96
	3618	100.00	

The formation of the 12 : 5 from the 10 : 4 salt is easily explained, as well as the separation of the tungstic sulphide, since we have

$$2(10WO_3 . 4Na_2O) + 5H_2S = 12WO_3 . 5Na_2O + 3WO_3 . Na_2O + 5WS_2 + 5H_2O.$$

A concentrated solution of the 10 : 4 sodium salt is resolved by boiling into the 12 : 5 salt and other compounds difficult to isolate in a state of purity. When a hot solution of potassic bromide or nitrate is added to a boiling solution of the 10 : 4 sodium salt, a white crystalline precipitate is speedily formed, which has the formula

$$12WO_3 . 5K_2O + 10aq.$$

But if a cold solution of a potassic salt is added to a cold solution of the 10 : 4 sodium salt, a white crystalline precipitate is formed, which has the formula

$$10WO_3 . 4K_2O + 9aq.$$

Twelve to Five Sodium Salt.—This is the salt to which Scheibler gives the formula

$$7WO_3 . 3Na_2O + 16aq.$$

and which Marignac writes

$$12WO_3 . 5Na_2O + 28aq.$$

According to Lotz, the salt contains fourteen atoms of water in place of sixteen as found by Scheibler. I have adopted the formula of Marignac, which agrees best with the analyses. In preparing this salt I have employed Scheibler's method, which consists in nearly neutralizing a boiling solution of the neutral tungstate, $WO_4Na_2 + 2aq.$ by chlorhydric acid. When the proper quantity of chlorhydric acid is added, the 12 : 5 salt is formed at once, and crystallizes from the solution in large colorless crystals, which, according to Scheibler, are

monoclinic; according to Marignac, triclinic. If the proportion of chlorhydric acid is just sufficient to give an onion-red reaction with litmus, crystals are obtained, which are either a combination or a mixture of equal molecules of the 10 : 4 and 12 : 5 salts. These crystals are, according to Dr. Gooch, triclinic; their habitus resembles that of the 12 : 5 rather than that of the 10 : 4 salt. In this salt, in two different preparations carefully dried and pressed with woollen paper,

I.	1.2546 gr. gave	0.9725 gr.	WO_3	= 77.51 p. ct.
	1.2320 gr. "	0.9554 gr.	"	= 77.55 "
	1.4680 gr. lost	0.2035 gr.	water	= 13.86 "
	1.7511 gr. "	0.2431 gr.	"	= 13.88 "
II.	1.0842 gr. gave	0.8407 gr.	WO_3	= 77.54 "
	1.0908 gr. "	0.8450 gr.	"	= 77.47 "
	1.6919 gr. lost	0.2362 gr.	water	= 13.96 "
	1.5259 gr. "	0.2125 gr.	"	= 13.93 "

The analyses agree closely with the formula

$$12WO_3 . 5Na_2O + 10WO_3 . 4Na_2O + 51aq.$$

or,

$$22WO_3 . 9Na_2O + 51aq.$$

which requires

		Calc'd.	Mean.	Found.			
$22WO_3$	5104	77.57	77.52	77.51	77.55	77.54	77.47
$9Na_2O$	558	8.48	8.57	...	...	...	...
$51H_2O$	918	13.95	13.91	13.86	13.88	13.96	13.93
	6580	100.00	100.00				

I have already stated that in repeated trials I had not been able to obtain sodic ditungstate described and analyzed by Lefort, though the process given by him was followed implicitly. In one experiment the crystals obtained gave on analysis results which correspond closely with the formula

$$12WO_3 . 5Na_2O + 28\ aq.$$

1.9868 gr. lost on ignition	0.2786 gr.	water	= 14.02 per ct.
1.2870 gr. " "	0.1806 gr.	"	= 14.01 "
0.9365 gr. gave	0.7243 gr.	WO_3	= 77.34 "
1.3560 gr. "	1.0483 gr.	"	= 77.31 "

	Calc'd.	Found.
$12WO_3$	77.38	77.34 77.31
$5Na_2O$	8.61	8.66
$28H_2O$	14.01	14.02 14.01
	100.00	

In this experiment the normal tungstate was dissolved in cold water to a very strong solution, glacial acetic acid was added in excess, and the whole allowed to stand for twenty-four hours, when prismatic crystals separated. In a second experiment a concentrated solution of sodic tungstate was heated to the boiling point and ordinary acetic acid added in excess. Alcohol then threw down a pasty mass, which, after re-solution in water and crystallization, gave on analysis results which corresponded with the formula

$$22WO_3 . 9Na_2O + 51 \text{ aq.}$$

1.0861 gr. lost on ignition	0.1492 gr. water	= 13.74 p. ct.
1.3830 gr. " "	0.1895 gr. "	= 13.70 "
0.8884 gr. gave	0.6899 gr. WO_3	= 77.66 "
1.2746 gr. "	0.9902 gr. "	= 77.69 "

	Calc'd.	Found.
$22WO_3$	77.57	77.67 77.69
$9Na_2O$	8·48	8.60
$51H_2O$	13.95	13.70 13.74
	100.00	

The small differences between the calculated formula and the direct results of the analyses, in this instance, are exactly such as would be produced by the admixture of a small percentage of the 10 : 4 sodium salt, which, as I have shown above, is formed when a solution of neutral sodic tungstate is boiled for some time with an excess of acetic acid. The general result of my own study of the action of acetic acid upon the neutral tungstate is, that we obtain the 12 : 5, the 22 : 9, or the 10 : 4 salt, according to the circumstances of the case, the constitution of the salt formed depending mainly upon the degree of concentration of the acid and upon the duration of its action. These results are in no way inconsistent with those of Lefort, and his analyses seem to leave no

reasonable doubt that he obtained various salts to be classed as ditungstates and tritungstates.

Potassic Tungstates.— When a hot solution of the 10 : 4 sodium salt is mixed with a hot solution of potassic nitrate, a white precipitate shortly appears in small colorless crystalline scales, which may be recrystallized by projecting them in very small quantities at a time into boiling water. This method, which was first given by Scheibler, enables us to redissolve the salt in water without loss from the excessively violent succussions which occur on heating the salt with water in the usual manner. The salt requires a rather large quantity of water for solution, and crystallizes almost completely from the cold liquid. Of this salt in the first preparation,—

0.9888 gr.	lost on ignition	0.0510 gr.	water	=	5.18 p. ct.
0.6513 gr.	" "	0.0358 gr.	"	=	5.49 "
1.1663 gr.	" "	0.0610 gr.	"	=	5.23 "
1.1287 gr.	" "	0.0596 gr.	"	=	5.28 "
1.0068 gr.	gave	0.8173 gr.	WO_3	=	81.21 "

In a second preparation,—

1.4312 gr.	lost on ignition	0.0751 gr.	water	=	5.25 p. ct.
1.5846 gr.	" "	0.0832 gr.	"	=	5.25 "
0.5786 gr.	gave	0.4686 gr.	WO_3	=	80.99 "
0.4773 gr.	"	0.3875 gr.	"	=	81.20 "
1.8957 gr.	"	1.5370 gr.	"	=	81.08 "

These analyses lead to the formula

$$12WO_3 . 5K_2O + 10aq.$$

which requires:—

		Calc'd.	Mean.	Found.			
				1.	2.		
$12WO_3$	2784	81.02	81.12	81.21	80.99	81.20	81.08
$5K_2O$	472	13.73	13.62	...	...	...	...
$10H_2O$	180	5.25	5.26	5.29*	5.25	5.25	...
	3436	100.00					

Marignac gives eleven molecules of water. Scheibler gives the formula $7WO_3 . 3K_2O + 6aq.$, but his analyses agree better with that of Marignac.

* Mean of the four determinations of water in the first preparation.

When normal potassic tungstate, WO_4K_2, is evaporated to dryness with boric hydrate, and the soluble salts are washed out from the mass, a salt is obtained which after recrystallization has the formula

$$10WO_3 . 4K_2O + 9aq.$$

The same salt is formed when cold solutions of potassic nitrate or bromide are added to cold solutions of the 10 : 4 sodium salts. It resembles the 12 : 5 potassium salt, already described, so closely that it is difficult to distinguish between the two. This salt has not been described by other writers upon the subject. In preparation *a*, from the action of boric acid upon normal potassic tungstate,

0.4566 gr. gave	0.3714 gr. WO_3	= 81.34 p. ct.
0.5915 gr. lost on ignition	0.0331 gr. water	= 5.59 "

In preparation *b*, from the action of acetic acid upon the normal potassium salt,

0.7418 gr. gave	0.6024 gr. WO_3	= 81.21 p. ct.
1.1104 gr. lost on ignition	0.0610 gr. water	= 5.49 "
0.7060 gr. gave	0.5736 gr. WO_3	= 81.27 "
1.0266 gr. lost on ignition	0.0556 gr. water	= 5.42 "

These analyses correspond best with the formula

$$10WO_3 . 4K_2O + 9aq.$$

		Calc'd.	Mean.			
$10WO_3$	2320	81.13	81.27	81.34	81.2	81.27
$4K_2O$	377.6	13.20	13.23	13.07	13.30	13.31
$9H_2O$	162	5.67	5.50	5.59	5.49	5.42
	2859.6	100.00				

It is probable that the salt had lost a little water by efflorescence. When normal potassic tungstate is dissolved in boiling water, it is decomposed into free alkali and 12 : 5 acid tungstate. The decomposition may be represented by the equation,

$$12(WO_3 . K_2O) + 7H_2O = 12WO_3 . 5K_2O + 14KHO.$$

In the acid salt formed in this manner,

0.7738 gr. lost on ignition	0.0414 gr. water	= 5.35 p. ct.
1.0385 gr. gave	0.8411 gr. WO_3	= 80.99 "

The formula $12WO_3 . 5K_2O + 10aq.$ requires 81.02 p. ct. WO_3 and 5.25 p. ct. H_2O.

Ammonic Tungstates.—When a solution of ammonic chloride is added to one of the 10 : 4 sodic tungstate, beautiful white talcose scales are thrown down, which are but slightly soluble in cold water. After washing, they may be dissolved in boiling water without evolution of ammonia and recrystallized. The analyses of this salt agree fairly well with the formula

$$10WO_3 . 4Na_2O + 4\{10WO_3 . 4(NH_4)_2O\} + 50aq.$$

as the following analyses show:—

I. { 0.5658 gr. gave 0.4851 gr. WO_3 = 85.74 p. ct.
0.5602 gr. lost on ignition 0.0690 gr. water and ammonia = 12.31 p. ct.

II. { 0.3346 gr. lost 0.0427 gr. water and ammonia = 12.77 p. ct.
0.3849 gr. gave 0.3294 gr. WO_3 = 85.59 p. ct.

		Calc'd.	Mean.	Found.	
$50WO_3$	11600	85.42	85.62	85.74	85.59
$4Na_2O$	248	1.83	1.79	1.94	1.64
$16(NH_4)_2O$	832	6.12	12.54	12.31	12.77
$50H_2O$	900	6.63			
	13580	100.00	99.95		

Analyses (I.) and (II.) are of different preparations of the same salt. When commercial ammonic tungstate (containing a little sodic oxide) is dissolved in ammonia, and acetic acid is added to the filtered liquid, a white, slightly soluble salt is obtained, which after recrystallization has the formula

$$12WO_3 . 5(NH_4)_2O + 6aq.$$

In this salt,

0.9293 gr. lost on ignition 0.1087 gr. = { 11.69 p. ct. NH_3 and H_2O
88.31 p. ct. WO_3

0.5366 gr. lost on ignition 0.0626 gr. = { 11.66 p. ct. NH_3 and H_2O
88.34 p. ct. WO_3

0.6602 gr. gave 0.2039 gr. platinum = 8.15 p. ct. $(NH_4)_2O$
1.1241 gr. " 0.3370 gr. " = 7.92 " "

		Calc'd.	Mean.	Found.	
$12WO_3$	2784	88.32	88.32	88.34	88.31
$5(NH_4)_2O$	260	8.24	8.03	8.15	7.92
$6H_2O$	108	3.44	3.64	3.51	3.77
	3152	100.00	99.99		

Marignac found in this salt five molecules of water. Lotz and Scheibler gave it the formula

$$7WO_3 . 3(NH_4)_2O + 3H_2O.$$

Marignac has also described and analyzed an ammonium salt to which he gives the formula

$$5WO_3 . 2(NH_4)_2O + 5H_2O.$$

I should double this formula, and write it

$$10WO_3 . 4(NH_4)O + 10H_2O,$$

so that it would then belong to the series of 10 : 4 salts, the existence of which I have endeavored to establish. According to Marignac, it breaks up by solution in water into the 12 : 5 and 8 : 3 salts.

$$2\{10WO_3 . 4(NH_4)_2O\} = 12WO_3 . 5(NH_4)_2O + 8WO_3 . 3(NH_4)_2O.$$

Zinc Salts.—When a solution of zincous sulphate is added in small excess to a hot solution of the 10 : 4 sodic tungstate, no precipitate is produced at first, but after a few seconds beautiful aggregates of white needles make their appearance, and continue to be deposited for some time. They are almost perfectly insoluble in boiling water. For analysis they were washed with cold water and dried in pleno over sulphuric acid. The zinc salt is soluble both in an excess of zincous sulphate and of sodic tungstate; hence the precipitate which is at first formed is instantly redissolved and does not become permanent until a small excess of the sulphate is added. In this salt,

0.3342 gr. lost on ignition	0.0349 gr. water	= 10.44 p. ct.
0.6392 gr. gave	0.5128 gr. WO_3	= 80.50 "
1.0205 gr. "	0.8200 gr. "	= 80.35 "

These analyses correspond with the formula

$$6WO_3 . 2ZnO + 10aq.$$

		Calc'd.	Found.	
$6WO_3$	1392	80.27	80.50	80.35
$2ZnO$	162	9.34	9.14 (loss)	
$10H_2O$	180	10.39	10.44	
	1734	100.00		

From this it appears that the zinc salt is formed by the decomposition of the 10 : 4 sodic tungstate. The result may be expressed by the equation,

$$10WO_3 . 4Na_2O + 4SO_4Zn = 6WO_3 . 2ZnO + 2\{2WO_3 . ZnO\} + 4SO_4Na_2.$$

The zincous ditungstate, as Lefort has shown, is readily soluble in water and remains in solution.

When a cold solution of zincous sulphate is added to a cold solution of the 10 : 4 sodium salt, a different result is obtained. A white precipitate is at first formed as before, which instantly redissolves. After a small excess of the sulphate has been added, the solution gives in a short time colorless needles of a second zinc salt. Like the 6 : 2 salt first described, this is insoluble in water, cold or hot, but readily dissolves in an excess of the tungstate or sulphate. When a large excess of the sulphate is present, the zincous tungstate does not separate from the solution. Of this salt in one preparation, dried over SO_4H_2:

0.6586 gr. lost on ignition	0.0706 gr. water	= 10.72 p. ct.
0.5894 gr. gave	0.0638 gr. ZnO	= 10.82 "
	0.4606 gr. WO_3	= 78.16 "

These analyses lead to the formula

$$10WO_3 . 4ZnO + 18aq.$$

which requires

		Calc'd.	Found.
$10WO_3$	2320	78.16	78.16
$4ZnO$	324	10.92	10.82
$18H_2O$	324	10.92	10.72
	2968	100.00	99.70

In a second preparation of the same salt, dried by woollen paper, 1.0006 gr. gave by ignition 0.1663 gr. water, also 0.7322 gr. WO_3 and 0.1048 gr. ZnO = 16.62 p. ct. water, 73.18 p. ct. WO_3, and 10.47 p. ct. ZnO.

These results correspond to the formula

$$10WO_3 . 4ZnO + 29aq.$$

which requires

		Calc'd.	Found.
$10WO_3$	2320	73.27	73.18
$4ZnO$	324	10.24	10.47
$29H_2O$	522	16.49	16.62
	3166	100.00	100.27

When a cold solution of zincous sulphate is added to a cold solution of the 22-atom sodium salt a precipitate is formed, which redissolves precisely as in the last-mentioned cases. After the solution of zinc has been added in small excess, white needles separate, which are insoluble in water, and have the formula

$$22WO_3 . 9ZnO + 66aq.$$

as the following analyses show:

1.4620 gr. gave 0.2509 gr. water on ignition, 1.0602 gr. WO_3 and 0.1508 gr. ZnO = 17.16 p. ct. water, 72.52 p. ct. WO_3, and 10.31 p. ct. ZnO.

		Calc'd.	Found.
$22WO_3$	5104	72.69	72.52
$9ZnO$	729	10.38	10.31
$66H_2O$	1188	16.93	17.16
	7021	100.00	99.99

The salt was dried for some time upon woollen paper.

General Conclusions.—From my own investigations, as well as from those of other chemists who have preceded me, I arrive at the following classification of the alkaline tungstates as most nearly representing the present state of our knowledge. There are three series of salts, which may be termed respectively normal tungstates, metatungstates, and pyrotungstates. The two first-named series may be represented by the following as typical salts:—

Normal Series.

$WO_3 . Na_2O + 2aq$	
$2WO_3 . Na_2O + 6aq$	Lefort.
$3WO_3 . Na_2O + 4aq$	"

Meta-Tungstates.

$4WO_3 . NaO_2 + 10aq$	or	$W_4O_{11}(NaO)_2 + 10aq$	Scheibler
$6WO_3 . 2BaO + 12aq$	"	$W_6O_{16}(BaO_2)_2 + 12aq$	"
$8WO_3 . 3(NH_4)_2O + 8aq$	"	$W_8O_{21}(NH_4O)_6 + 8aq$	Marignac
$10WO_3 . 4Na_2O + 23aq$	"	$W_{10}O_{26}(NaO)_8 + 23aq$	
$12WO_3 . 5Na_2O + 28aq$	"	$W_{12}O_{31}(NaO)_{10} + 28aq$	Marignac
$14WO_3 . 6Na_2O + 42aq$	"	$W_{14}O_{36}(NaO)_{12} + 42aq$	"

The salts of the normal series require no special notice. As already stated, I have not succeeded in preparing the di- and tri-salts of Lefort, but there seems to be no reason to doubt their existence. The pyro-salts are obtained from the meta-salts by ignition, as insoluble crystalline masses, which are decomposed by long boiling with water. All the meta-tungstates with an alkaline base, appear to contain water of constitution and to have an acid reaction, but it is difficult to determine the quantity of basic hydrogen with certainty, and the mere fact that the salts have an acid reaction is not in itself conclusive evidence that they are in the strict chemical sense *acid.* Tungstates have been described by different chemists which do not fall within either of the groups given above. In all these cases, however, it will be found on examination, that the analyses do not agree well with the formulas assigned, and that there is reason to believe that the salts studied were mixtures. I consider it at least probable that the tri-salts of Lefort belong in reality to the meta-series, their molecular weights being doubled. But it is of course possible that we have here cases of isomerism, and I much regret that I did not succeed in obtaining these salts for study and comparison. With respect to the double salt which I have described above, and which has the formula

$$12WO_3 . 5Na_2O + 10WO_3 . 4Na_2O + 51aq.$$

I may remark that it is possible that the compound is really

$$22WO_3 . 9Na_2O + 51aq.$$

and that it is not a double salt, but one term in a series which we obtain by again doubling the formulas of the meta-tungstate as I have given them above. The question is one which I must leave undecided for the present at least.

The analogy between the compounds of tungsten and

molybdenum is in general so great, that we ought to expect to find alkaline molybdates corresponding to the three series of tungstates. We owe to Ullik the most complete examination of the molybdates which has been published. A careful study of his results will show that, while we have a number of molybdates to which there are apparently no corresponding tungstates, we have at least reason to believe in the existence of the three series of normal, meta, and pyro salts. Thus the following salts may be assumed as typical:—

Normal Series.

$MoO_3 . Na_2O + 2aq$

$2MoO_3 . Na_2O$ and with $1 . H_2O$

Meta Series.

$4MoO_3 . Na_2O + 6aq$	or	$Mo_4O_{11}(NaO)_2 + 6aq$
$6MoO_3 . 2Na_2O + 14aq$	"	$Mo_6O_{16}(NaO)_4 + 14aq$
$8MoO_3 . Na_2O . 2H_2O + 2aq$	"	$Mo_8O_{21}(NaO)_2(HO)_4 + 2aq$
$10MoO_3 . Na_2O . 3H_2O + 9aq$	"	$Mo_{10}O_{26}(NaO)_2(HO)_6 + 9aq$
$14MoO_3 . 6Na_2O + 44aq$	"	$Mo_{14}O_{36}(NaO)_{12} + 44aq$
$16MoO_3 . 2Na_2O . 5H_2O + 3aq$	"	$Mo_{16}O_{41}(NaO)_4(HO)_{10} + 3aq$
$18MoO_3 . 2BaO . 6H_2O + 2aq$	"	$Mo_{18}O_{46}(BaO_2)_2(HO)_{12} + 2aq$

It may of course be maintained that the arrangement of the acid salts of molybdic oxide which I have adopted is purely arbitrary, and that they might be written with equal or greater probability in the usual manner, as members of the normal series, which would then be:

$MoO_3 . Na_2O + 2aq$	$8MoO_3 . Na_2O + 2aq$
$2MoO_3 . Na_2O + aq$	$9MoO_3 . BaO + 4aq$
$3MoO_3 . Na_2O + 7aq$	$10MoO_3 . Na_2O + 12aq$
$4MoO_3 . Na_2O + 6aq$	$16MoO_3 . Na_2O + 9aq$

To this I reply that one arrangement is no more arbitrary than the other, since we have no positive knowledge of the constitution of these salts, their molecular weights being, as in the case of most inorganic compounds, entirely unknown. The commonly received view is therefore also a pure assumption. In any case, however, we have the two salts represented respectively by the formulas

$4MoO_3 . Na_2O + 6aq$	or	$Mo_4O_{11}(NaO)_2 + 6aq$
$14MoO_3 . 6Na_2O + 44aq$	"	$Mo_{14}O_{36}(NaO)_{12} + 44aq,$

forming the upper and lower limits of a molybdic series corresponding to alkaline tungstates, and from these we may fairly infer the existence of the intermediate compounds. But one acid tungstate of the meta series is at present known, the salt

$$8WO_3 . Na_2O + 12aq, \quad \text{or} \quad W_8O_{25}(NaO)_2 + 12aq.$$

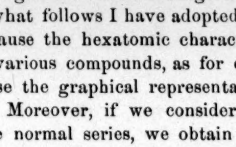
This may be considered as an acid salt of the 8-atom term, and written

$$8WO_3 . Na_2O . 2H_2O + 10aq,$$

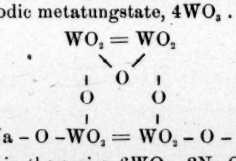
so that it will correspond with the molybdic salt

$$8MoO_3 . Na_2O . 2H_2O + 2aq.$$

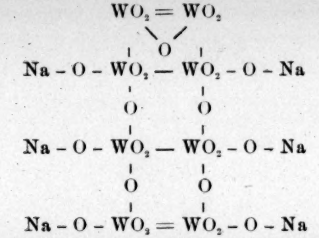
But the supposition that acid metatungstates of the 4 : 1 series really exist is in no way inconsistent with the view of the whole subject which I have taken. So far as I know, no attempt has been made to exhibit the mode of union of the elements in the higher tungstates. Our views of the subject will differ according as we consider tungsten as tetratomic or hexatomic. In what follows I have adopted the latter hypothesis, partly because the hexatomic character of tungsten is well marked in various compounds, as for example in WCl_6, and partly because the graphical representations are, on the whole, simpler. Moreover, if we consider tungsten to be tetratomic in the normal series, we obtain a reason for the existence and peculiar character of the meta series, by supposing that in this the metal is hexatomic. We may, to begin with, represent sodic metatungstate, $4WO_3 . Na_2O$, as follows:



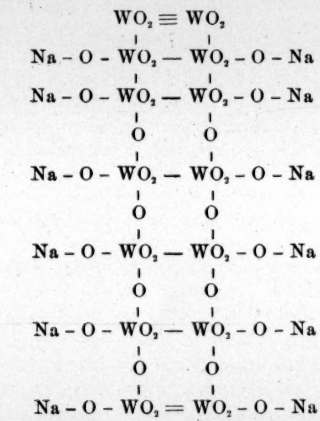
The next term in the series, $6WO_3 . 2Na_2O$, will then be



The third term, $8WO_3 . 3Na_2O$, may be represented by the graphical formula

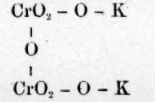


and so on for the other known terms, the highest, $14WO_3 . 6Na_2O$, being represented by the expression



It will be seen that, with this view of the subject, those terms in the series in which the number of atoms of sodic oxide is even are represented by formulas in which the free atoms of WO_2 are united, in part directly, and in part by oxygen, while the union is direct when the number of atoms of sodic oxide is odd. I shall return to this subject in speaking of the phosphotungstates and other complex inorganic

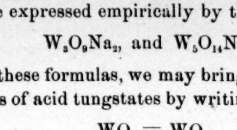
acids. No great value can, in the present state of our knowledge, be attributed to formulas like the above. They afford, however, some assistance in showing the possible mode of formation of the different terms of the series, but various other constructions may be devised which are perhaps equally probable. In adopting provisionally the particular construction which I have used, I have simply followed the clew given by the commonly received formula for potassic dichromate,



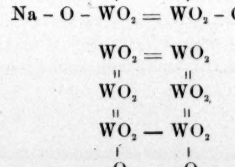
which of course gives a similar expression for the homologizing term in the acid tungstate series. So far as I am aware, no attempt has been made to formulate the remarkable compounds of tungsten described by Wœhler and others, and which may be expressed empirically by the formulas

$$W_3O_9Na_2, \text{ and } W_5O_{14}Na_2.$$

If we double these formulas, we may bring them into harmony with the series of acid tungstates by writing them respectively,



and



These formulas, if like the others purely hypothetical, have at least the merit of explaining the production of the insoluble sodium salts in a simple and natural manner. They are also entirely consistent with the simplest view which we can adopt with respect to the constitution of the blue oxide of tungsten, which is commonly written W_2O_5, but which is much more probably W_4O_{10}, and structurally

$$\begin{array}{ccc} WO_2 & - & WO_2 \\ | & & | \\ O & & O \\ | & & | \\ WO_2 & - & WO_2. \end{array}$$

The progress of science tends to show that the constitution of inorganic compounds is more complex than would at first appear. It would not be difficult to multiply instances which support this view, but I shall content myself with citing a single case, which has not been discussed, and which, strangely enough, has attracted but little attention. I refer to the remarkable series of compounds of molybdenum studied by Blomstrand* and by Atterberg.† Representative terms in this series are expressed by the formulas

$Mo_3Cl_4 . Cl_2$	$Mo_3Cl_4 . (OH)_2$	$Mo_3Cl_4 . Br_2$
$Mo_3Br_4 . Br_2$	$Mo_3Br_4 . (OH)_2$	$Mo_3Br_4 . SO_4$

omitting water of crystallization for greater brevity. The action of alkalies upon the bromide $Mo_3Br_4 . Br_2$ produces first $Mo_3Br_4 . (OH)_2$, and afterward $Mo_3(OH)_4(OH)_2$, or $Mo_3(OH)_6$, the hydrate of the protoxyde of molybdenum, usually written $MoO . OH_2$, or $Mo(OH)_2$. There is therefore good reason to believe that the lowest expression for this hydrate is $Mo_3(OH)_6$, the structural formula of the corresponding bromide being, perhaps

$$\begin{array}{c} Mo = Br_2 \\ \| \\ Mo = Br_2 \\ \| \\ Mo = Br_2 \end{array}$$

In this formula the end atoms of molybdenum are tetratomic, and the middle atom hexatomic, which will perhaps

* Journal fuer prakt. Chemie, 82, 436.

† Nagra bidrag till Kännedomen om Molybden, Stockholm, 1872. p. 16.

explain the fact that there are but two movable atoms of bromine in a whole series of salts. If molybdic protoxide is Mo_2O_3, it is probable that the teroxide is not MoO_3, but rather some higher multiple of this expression, and we may extend the inference to WO_3 also.

With these preliminaries, I pass to the special subject of my work.

[*To be continued.*]

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

No. II.

ON SOME COMPOUNDS OF AROMATIC AMINES WITH SILVER NITRATE AND SULPHATE.

By W. G. Mixter.

A few compounds of silver nitrate with amido substances in the benzol series have been made, but no special importance appears to have been attached to them. Griess* found that one molecule of azodiphenyl-diamine united with silver nitrate to form $C_{12}H_{11}N_3AgNO_3$, and he also obtained the azobromodiphenyl-diamine product $C_{12}H_9Br_2N_3AgNO_3$. Hofmann† found that two molecules of melaniline united with one molecule of silver nitrate.

It seemed an object to prepare some compounds with the aromatic monamines, and the following are some of the results.

Aniline Silver Sulphate.

5 grams of silver sulphate and 6 grams of aniline were dissolved in boiling water. Some silver was reduced, and there was a dark residue. The filtrate from the hot solution

* Liebig's Ann. 121, 257. † Liebig's Ann. 67, 129.

gave on cooling a mass of hair-like rose-tinted crystals, whose color was probably due to the reddish tint of the mother liquor. The product was washed with water and dried to a constant weight over caustic potash. The analysis shows a compound corresponding to silver sulphate with four molecules of aniline and two molecules of water.

		Calculated for $(C_6H_5NH_2)_4Ag_2SO_4, 2H_2O$.	Found.
C	...	40.00	39.82
H	...	4.45	4.56
N	...	7.78	7.73
Ag	...	30.00	30.06
S	...	4.44	4.47
O	...	13.33	...
		100.00	

The substance lost *in vacuo* over oil of vitriol in four days 33.08 p. ct. Two molecules each of aniline and water are equal to 30.83 p. ct. Absolute alcohol removes the larger portion of aniline from the aniline silver sulphate and leaves a residue which reacts for aniline. A product from commercial aniline thus treated left a residue in which the silver found was 53 p. ct. $C_6H_7NAg_2SO_4$ has 53.3 p. ct. of silver.

Paratoluidine Silver Sulphate.

6 grams of solid toluidine and 4.5 grams of silver sulphate gave by the method above described an analogous compound of the same appearance as the aniline silver sulphate.

		Calculated for $(C_7H_7NH_2)_4Ag_2SO_4, 2H_2O$.	Found.
C	...	43.30	43.02
H	...	5.15	5.22
N	...	7.22	7.14
Ag	...	27.83	27.79
S	...	4.12	4.16
O	...	12.38	...
		100.00	

Absolute alcohol removes all the toluidine from the substance and leaves silver sulphate.

Metanitraniline Silver Nitrate.

13 grams of metanitraniline (m. p. 110° C) were dissolved in boiling absolute alcohol, and added to a boiling solution of 2 grams of silver nitrate in absolute alcohol. The slight precipitate which formed was filtered off and the solution was rapidly cooled. The mass of hair-like yellow crystals was washed with absolute alcohol and dried over oil of vitriol.

		Calculated for $(C_6H_4NO_2NH_2)_4AgNO_3$.	Found.
C	...	39.89	39.72
H	...	3.32	3.43
N	...	17.45	17.35
Ag	...	14.96	15.11
O	...	24.38	...
		100.00	

Metanitraniline silver nitrate melts without decomposition at 124°–125° C. Cold water completely removes the silver nitrate and leaves metanitraniline.

Nitrotoluidine Silver Nitrate.

8 grams of nitrotoluidine (m. p. 77.5°) were dissolved in boiling water, and a solution of 2.5 grams of silver nitrate was added; the small black decomposition product was filtered off and the solution cooled. The greenish-yellow crystalline product was washed with water, and dried over oil of vitriol.

		Calculated for $(C_7H_6NO_2NH_2)_4AgNO_3$.	Found.
C	...	43.20	42.81
H	...	4.11	4.28
N	...	16.19	16.06
Ag	...	13.88	13.98
O	...	22.62	...
		100.00	

The substance melts without decomposition at 131°–132°C., and is soluble in absolute alcohol. Its aqueous solution evaporates spontaneously in light without decomposition, and paper

saturated with it is not darkened by sunlight. Equal weights of silver nitrate and nitrotoluidine gave the same compound.

Paratoluidine Silver Nitrate.

A hot clear aqueous solution of solid toluidine was gradually added to a cold solution of silver nitrate, which was constantly agitated and kept cold to prevent decomposition. The almost white crystalline product was washed with water.

		Calculated for $(C_7H_7NH_2)_2AgNO_3$.	Found.
C	...	43.75	43.52
H	...	4.68	4.79
N	...	10.94	10.85
Ag	...	28.13	28.17
O	...	12.50	...
		100.00	

It melts with decomposition at 101°C. When treated with absolute alcohol it slowly decomposes with the separation of a brownish mass.

From 6 grams of a liquid marked β-toluidine and 2 grams of silver nitrate a product was obtained which gave no formula.

		Calculated for $(C_7H_7NH_2)_4AgNO_3$	Found.
C	...	56.19	53.89
H	...	6.02	5.94
N	...	11.71	...
Ag	...	18.06	19.88
O	...	8.02	...
		100.00	

The atomic ratio of the carbon to the hydrogen is as 7 to 9.27, corresponding within the limits of the errors of analysis to that of toluidine. Another experiment gave similar results. The quantity of liquid toluidine at command was too small to test its purity. It boiled at 195°–198° C. The results indicate that the liquid toluidine contained some of the solid modification, and that the substance analyzed was a mixture of $(C_7H_7NH_2)_4AgNO_3$ and $(C_7H_7NH_2)_2AgNO_3$.

Aniline silver sulphate $(C_6H_5NH_2)_4Ag_2SO_4, 2H_2O$.
Paratoluidine silver sulphate $(C_7H_7NH_2)_4Ag_2SO_4, 2H_2O$.
Metanitraniline silver nitrate $(C_6H_4NO_2NH_2)_4AgNO_3$.
Nitrotoluidine silver nitrate $(C_7H_6NO_2NH_2)_4AgNO_3$.
Paratoluidine silver nitrate $(C_7H_7NH_2)_2AgNO_3$.

The first two compounds without the water of crystallization, are analogous to the ethylidenamine* and the ammonia compounds of silver sulphate; the paratoluidine silver nitrate is similar to $(NH_3)_2AgNO_3$. The nitraniline silver nitrate and the toluidine silver nitrate contain one more ammonia group than was known to join to silver nitrate, and it is worthy of notice that nitraniline and toluidine are weak bases. In making the five bodies, excepting the nitraniline silver nitrate, an excess of the silver salt was used, hence the work does not decide whether more molecules of these amines will join a molecule of the silver salts. When ammonia is added to solutions of silver sulphate and of silver nitrate, a precipitate forms at first; but the five amines when added to an excess of the silver salts in dilute solutions, do not cause turbidity even after some hours, except in case of the toluidine, which at first produces no turbidity, but slowly gives a brown precipitate. This reaction, and the fact that two of the bodies are completely separated by simple solvents into the constituents from which they were made, indicate that the substances are "molecular compounds," similar to hydrous salts. The writer is aware that the constitution of a large number of bodies resulting from the union of ammonia or amines with metallic salts, can best be explained by supposing that the metal is joined to pentad nitrogen, and that the nitrogen atoms join each other. The present theory of valence does not explain the constitution of double salts or of hydrous salts, and there is no proof as yet that it explains the ammonia and amine addition products with metallic salts.

*Am. Jour. 17, 427.

No. III.

ON CLARKE'S METHOD FOR THE SEPARATION OF TIN FROM ARSENIC AND ANTIMONY.

By Fred. P. Dewey.

In the beginning of the year 1876 an investigation was undertaken on the separation of tin, arsenic and antimony. After some study on the published methods and some work on a few of them, it was decided to make a thorough investigation of the method proposed by F. W. Clarke,* as that seemed the most favorable method notwithstanding the poor results obtained by G. C. Wittstein.† Clarke's method is to add to the solution of the metals prepared as for the precipitation of sulphides, oxalic acid in the proportion of twenty parts to one part of tin, keeping the solution so concentrated that oxalic acid will separate in the cold. Hydrogen sulphide gas is then passed through the boiling solution until the antimony and arsenic are all precipitated, the solution is allowed to stand in a warm place for half an hour, the sulphides are filtered off and separated according to any of the well-known methods; the filtrate is neutralized by ammonia, the precipitate formed dissolved in ammonium sulphide, and acetic acid added in excess, whereby the tin is precipitated as a light colored mixture of sulphide and oxide which soon darkens in color. When complete precipitation is insured by standing in a warm place several hours, it is filtered off, washed in ammonium nitrate solution, ignited and weighed as stannic oxide, SnO_2. The results given by Clarke were the recovery of 99.93 and 99.57 p. ct. of the tin from solutions containing unknown amounts of antimony and arsenic, the latter result being considered poor by him, and owing to incomplete precipitation from filtering too soon after the addition of reagents. It was originally intended to investigate the separation of tin from antimony, and tin from arsenic separately, and then tin from antimony and arsenic; but it soon became evident that with the time at my disposal I could only undertake the

* Am. Jour. Sci. 49, 145 † Fresenius' Zeitschrift, 9, 487.

separation of tin from antimony, and the experiments here described were devoted entirely to that object.

I made two separations, intending to follow Clarke's plan exactly. Pure metallic antimony was weighed out and dissolved in strong hydrochloric acid with the addition of potassium chlorate. As soon as all the antimony had gone into solution, weighed amounts of pure metallic tin were added, and the final solution evaporated to dryness to drive off hydrochloric acid and decompose all potassium chlorate; the residue was taken up in a few drops of hydrochloric acid and water, and the requisite amount of oxalic acid added. As oxalic acid is soluble in ten parts of cold water*, one solution could not be over 55 cc. and the other over 39 cc., no account being taken of the few drops of hydrochloric acid added. Hydrogen sulphide was transmitted through the boiling solution for half an hour, when the antimony seemed to be all down. After standing for half an hour in a warm place, a portion of the fluid was run through a weighed filter, and the filtrate tested with hydrogen sulphide, when more antimony came down; this was filtered off and the second filtrate tested, when still more antimony came down. Thereupon I gave up the idea of keeping the solution so concentrated, and diluted it a little, when the antimony came down so that on testing the filtrate by diluting and adding more hydrogen sulphide no antimony was precipitated; the precipitate was filtered off, washed well, dried at 100°C. and weighed. The filtrate was diluted largely, ammonia added, the slight precipitate dissolved in ammonium sulphide, acetic acid added in excess, and the whole allowed to stand over night, when the precipitate was filtered off, washed in ammonium nitrate, ignited and weighed as stannic oxide, SnO_2.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.3089 gr.	0.2722 gr.	0.3063 gr.	0.2704 gr.
0.2671 "	0.1908 "	0.2704 "	0.1821 "

In a second set a portion of the antimony trisulphide was heated to 230°C. in a tube filled with dry carbon dioxide and the loss calculated for the whole precipitate.

* Storer's Dict. of Solubilities.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.1542 gr.	0.2705 gr.	0.1356 gr.	0.2717 gr.
0.1172 "	0.3736 "	0.1186 "	0.3760 "

Some qualitative experiments were undertaken to test the influence of free hydrochloric acid on the separation, and also the statement of Clarke that antimony could not be detected in the filtrate from the antimony trisulphide either by the Marsh test or the black stain on platinum with zinc, and that oxalic acid did not interfere with either of these tests. I found that oxalic acid obscured the platinum and zinc test by the formation of a dense white coating on both the platinum and zinc when the acid became nearly neutralized, (probably an oxalate of zinc) which completely masked any black stain that might have been produced on the platinum, but that it did not obscure the Marsh test in the least. Five solutions were prepared as before, each solution containing 0.2 gr. tin and 0.15 gr. antimony, and evaporated to dryness, the residues being taken up in oxalic acid; and, starting with no free hydrochloric acid, 1, 3, 5 and 7 cc. of hydrochloric acid of 1.09 sp. gr. were respectively added. These solutions were diluted to 250 cc. Hydrogen sulphide was transmitted through the boiling solutions for three-quarters of an hour, and the antimony trisulphide filtered off. The filtrates were tested in an ordinary Marsh apparatus.

No. 1 containing no HCl gave only a slight yellowish mirror, probably S.

No. 2 containing 1 cc. HCl gave a metallic mirror for about two minutes.

No. 3 containing 3 cc. HCl gave a good metallic mirror for some time.

No. 4 containing 5 cc. HCl gave a very good metallic mirror for a long time, about equal portions of the filtrates being used for each test.

No. 5 containing 7 cc. HCl deposited thin red flakes of Sb_2S_3 on concentration.

These results show, that to get the best separation no hydrochloric acid can be present, although a very small amount can be present without exerting any very great solv-

ent action on the antimony trisulphide.* The precipitates of antimony trisulphide were dissolved in strong hydrochloric acid, evaporated and treated with zinc; the metallic precipitates were treated with small amounts of dilute hydrochloric acid, filtered, and the filtrates tested with mercuric chloride, when heavy precipitates of mercurous chlorides came down in every case. These results show that it is always necessary to make double precipitations of the antimony, a point suggested by Clarke as being necessary only when great accuracy is required. The results of the above described experiments indicate that the following modifications of the original plan are required, viz: a solution *without free mineral acids*, and diluted to 250 cc. for 0.2 gr. of each metal; also in all cases a double precipitation of the antimony.

Solution in hydrochloric acid with potassium chlorate being rather tedious, a mixture recommended by Dr. Clemens Winkler in Fresenius' *Zeitschrift*, consisting of one part strong nitric acid, four parts strong hydrochloric acid, and five parts water, was tried and found very satisfactory. The evaporation of a solution of tin and antimony prepared by this mixture cannot safely be undertaken, on account of the well known fact that stannic chloride will volatilize from a dilute acid solution, and both stannic chloride and antimony trichloride from a concentrated acid solution on evaporation, and the use of an alkali to neutralize the acid is objectionable for reasons I shall state beyond; but, from the fact that in the analyses given the metals were dissolved in hydrochloric acid and potassium chlorate and evaporated to dryness without any very great loss on the total amount of metals used, it suggested itself that the presence of a sufficient amount of potassium chloride to form double salts with all of the tin and antimony used, would serve to fix the tin and antimony during evaporation. Two experiments were made to ascertain definitely whether tin or antimony would volatilize under such conditions. 1.7 gr. of tin were dissolved in 50 cc. of the aqua regia and 2.5 gr. of potassium chloride were added; the solution was transferred to a retort of 350 cc. capacity, diluted to 100 cc. and distilled at about 100°C. in an air bath, while a slow

*The poor results obtained by Wittstein were probably due to the presence of large amounts of free acid in his solutions.

current of air was forced through the retort. When half of the fluid had passed over, the receiver was removed, emptied and returned, then the distillation was resumed. The distillate was diluted to 100 cc., part of the acid was neutralized by sodium carbonate, and hydrogen sulphide was transmitted through it, when there was only a slight separation of sulphur, probably caused by chlorine given off from the aqua regia. The distillation was carried to dryness, the distillate treated in the same way and with the same result. A second portion of tin was treated in the same way omitting the addition of potassium chloride, and in each portion of the distillate, heavy precipitates of tin sulphide were obtained. 1.5 gr. of antimony were treated exactly as the tin in the first experiment with the same result. 1.5 gr. more of antimony were treated without potassium chloride. In the first distillate containing three-quarters of the liquid no antimony could be detected, but in the final distillate a large amount of antimony was found. These experiments show that solutions of stannic chloride and antimony trichloride containing free hydrochloric or nitric acid or both, can be safely evaporated to dryness if a sufficient amount of potassium chloride is present. In all of my subsequent analyses the free acid was removed by evaporation to dryness in the presence of an excess of potassium chloride.

The course next adopted was to dissolve about 0.2 gr. of each metal in the aqua regia, add sufficient potassium chloride and evaporate to dryness. The requisite amount of oxalic acid was then placed in the beaker and boiling water added until a clear solution was obtained, which is very easy to do. The solution was diluted to 250 cc. Hydrogen sulphide was transmitted through the boiling solution for half an hour. The precipitate was immediately filtered off* and washed. The precipitate of antimony trisulphide containing a little tin sulphide was dissolved in ammonium sulphide. This solution was poured into a boiling solution of oxalic acid, containing enough of the acid to decompose the ammonium sulphide, and still have sufficient excess to hold the tin in solution.

* It was observed that when the fluid with the Sb_2S_3 precipitate was allowed to stand to remove H_2S, there was always a separation all through the liquid of flakes which did not look like S, but did look like SnS_2; a supposition supported by the fact that these flakes separated in the filtrate from Sb_2S_3, filtered off immediately, as it cooled during filtering, and were dissolved again on applying heat.

Hydrogen sulphide was transmitted through the boiling solution for ten minutes, and the solution filtered through a weighed filter; the precipitate was well washed with hot water, dried at 100° C., weighed and a portion converted into pure anhydrous antimony trisulphide as before. The filtrates containing the tin were united and treated with the proper reagents; the precipitate was filtered off after standing, washed in ammonium nitrate and weighed as tin oxide. Each filtrate was always tested to insure complete precipitation.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.2243 gr.	0.2238 gr.	0.2390 gr.	0.2218 gr.
0.1908 "	0.2346 "	0.2058 "	0.2219 "
0.3871 "	0.2573 "	0.3949 "	0.2607 "
0.3108 "	0.2187 "	0.3158 "	0.2203 "

Repeated testings of the weighed tin and antimony indicated that the actual separations were satisfactory. There were, however, some difficulties and some obvious sources of error in the methods used for their determination which would cause gain of antimony and gain or loss of tin. On dissolving the antimony sulphide in strong hydrochloric acid, a black residue was always obtained, no matter how much the precipitate had been washed, indicating the presence of oxalic acid in the precipitate in some form. The solution of tin required extreme dilution to get it all down, the solution being diluted in one case to nearly 1500 cc., which seemed to be due to the unavoidable presence of large amounts of ammonium oxalate. Besides this the washing of the tin precipitate was very difficult and tedious indeed, which is a reason for keeping the amount of salts in the solution as small as possible.

To avoid the difficulty of precipitating the tin completely and washing it thoroughly, it seemed necessary to remove the oxalic acid entirely from the filtrates containing it. Strong sulphuric acid was decided upon as the best means, that is to evaporate the solution to dryness, and treat with strong sulphuric acid at about 100° C., which rapidly decomposes the oxalic acid into water, carbon monoxide and dioxide. In two experiments 0.5 gr. tin were dissolved in the aqua regia, potassium chloride was added, the solutions were evaporated

to dryness and the residues taken up in oxalic acid, 25 gr. in one and 30 gr. in the other. They were again evaporated to dryness and treated with about 40 cc. of strong sulphuric acid at 100° C. until all effervescence had ceased, when they were diluted to 500 cc., treated with hydrogen sulphide gas for half an hour and allowed to settle, after which the precipitates were filtered off, washed in ammonium nitrate and weighed as tin oxide, yielding 0.4998 and 0.4996 gr. tin. Applying this process to the filtrate from the antimony trisulphide, the following separations were next made, the process being conducted as before except the dilution of the solution before the precipitation of the antimony trisulphide to 400 cc., when 0.5 gr. of each metal were used.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.2000 gr.	0.2000 gr.	0.2084 gr.	0.1964 gr.
0.2000 "	0.2000 "	0.2030 "	0.2031 "
0.3000 "	0.3000 "	0.3070 "	0.3029 "
0.5000 "	0.5000 "	0.5066 "	0.5004 "
0.5000 "	0.5000 "	0.5177 "	0.4962 "

The last two antimony results were corrected for the carbonaceous residue, which was filtered off on a small filter and weighed, being 0.0085 and 0.0070 gr. Following the analogy of the two cases, we may suppose, as J. P. Cooke, jr.,* does in his determination of the atomic weight of antimony, that this residue comes from occluded oxalic acid.

A slight modification of Bunsen's† method of weighing antimony as antimony tetroxide having given 0.4996 and 0.4986 gr. antimony instead of 0.5000 gr., four separations were made in which the antimony was weighed as antimony tetroxide, the other details remaining as before.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.5000 gr.	0.5000 gr.	0.5190 gr.	0.4911 gr.
0.5000 "	0.5000 "	0.5067 "	0.4963 "
0.5000 "	0.5000 "	0.5136 "	0.4973 "
0.5000 "	0.5000 "	0.5146 "	0.4926 "

* Transactions of Amer. Acad. of Sci., Bost., 13, 15.
† Ann. der Chemie, 106, 3.

While the results obtained by this method are no better than those obtained by weighing antimony as trisulphide, yet it required less time and is a much neater operation to get them.

Since reaching the above results and conclusion Bunsen* has published further experiments on this method of weighing antimony, and reaches the conclusion that it cannot easily be done with accuracy, because more oxygen than is necessary will be driven off at a temperature only slightly above that required to convert antimony pentoxide into the tetroxide, and at a very intense heat the trioxide thus formed will be volatilized. From my results it would seem that the heat employed was too low rather than too high.

In conclusion, I desire to express my thanks to Prof. O. D. Allen for much kind assistance during the progress of the above work.

No. IV.

INFLUENCE OF ACETIC ACID ON THE SEPARATION OF IRON AS A BASIC ACETATE FROM MANGANESE, ZINC, COBALT AND NICKEL.

By John Jewett.

It has often been observed when manganese is separated from iron by precipitating the latter as a basic ferric acetate, that some manganese is carried down with the iron precipitate. Eggertz,† calling attention to this fact, stated that this trouble could be obviated, at least to a great extent, by the presence of free acid. To this end he recommends adding to a volume of 500 cc., after nearly neutralizing with sodium carbonate, 3 cc. of HCl (strength not given). Stœckmann communicated in Fresenius' *Zeit.* 1877, p. 172, the results of a series of experiments in separating iron from manganese in "Spiegeleisen" containing about 10 p. ct. of manganese. He found that varying, and, usually, very considerable amounts of manganese were precipitated along with the iron, in many

* Fresenius' Zeitschrift, 18, 268.

† Berg- und Huettenmænnische Zeitung, 1867, p. 187.

cases equalling 10 p. ct. of all that was present, and concludes that it is absolutely necessary to redissolve and reprecipitate the iron and recover the manganese in the second filtrate. He alluded to the modification recommended by Eggertz, but did not adopt it, finding the free acid made the iron precipitate difficult to wash. C. Krœmer* was astonished at these results, and states that the only precaution necessary (besides thorough washing) is the addition of one or two drops of dilute acetic acid to the previously neutralized solution, before adding sodium acetate and boiling; he found that at most only $\frac{1}{10}$ p. ct. of manganese goes down with the iron. The experience of G. Matzurke† was, on the other hand, quite like that of Stœckmann. He found, contrary to Krœmer, that the addition of one or two drops of dilute acetic acid made no appreciable difference in the results.

In view of these statements concerning a much used process, I have, with the advice of Prof. O. D. Allen, made some experiments to ascertain the influence of free acetic acid in this method of separating iron from manganese and the other metals, zinc, cobalt and nickel. As a basis of operation, solutions of Fe_2Cl_6 containing free HCl, and of $MnCl_2$, $ZnCl_2$, $Co(NO_3)_2$ and $Ni(NO_3)_2$ of known strength, (.2 gr. of the metals to every 100 cc. of solution) were made; then by uniting 100 cc. of the iron solution with the same amount of any one of the other solutions, a mixture of the desired metals to be separated was obtained. A few preliminary trials with iron and manganese gave results in accordance with the statements of both Stœckmann and Eggertz. Presence of free acid decreased the amount of manganese in the iron precipitate, but *too much* prevented complete precipitation of the iron. To ascertain to what extent free acetic acid is efficient in keeping manganese, likewise zinc, nickel and cobalt in solution, when present in quantities not too great to prevent precipitation and washing of the iron, necessitated a series of experiments, in which the only variable factor was the acetic acid. In every case, 2 gr. sodium acetate were used (an amount equal to ten times the weight of iron present), and the solutions were diluted to the same volume, viz: 300 cc. before boiling to separate iron. The precipitated iron was examined after thorough washing,

* Fresen. Zeit. 1877, p. 334. † Fresen. Zeit. 1878, p. 78.

by redissolving and repeating the separation, and testing the filtrate from the iron precipitate, according to whether Mn, Zn, Co or Ni was present, with Br, $NaCO_3$ or NaOH. The results are here tabulated:

P. ct. by volume of Acetic Acid (1.044 Sp. Gr.) added.	Taken Fe .2 gr. " Mn .2 " P. ct. of Mn in 2d Filtrate.	Taken Fe .2 gr. " Zn .2 " P. ct. of Zn in 2d Filtrate.	Taken Fe .2 gr. " Ni .2 " P. ct. of Ni in 2d Filtrate.	Taken Fe .2 gr. " Co .2 " P. ct. of Co in 2d Filtrate.
0	2.788	...	...	...
½	.697	2.849	1.888	...
1	.585	2.046	1.770	.590
2	.193	...	1.652	...
3	.154	...	1.468	...
4	Trace	0	1.219	.315
4	Trace	0	...	...
5	Trace	...	.314	...

It was found that 4 p. ct. by volume of acetic acid 1.044* sp. gr. has no appreciable bad effect on the separation and filtration of the iron; when 5 p. ct. is used its effect is sometimes apparent, but occasions no great trouble. On making some trials with over 5 p. ct., iron was not always completely precipitated, and was very difficult to wash. Great care was taken in these experiments to have as little free acid as possible present besides that intentionally added. This end can best be attained by adding sodium carbonate to the *cold* and preferably concentrated acid solution until a slight precipitate forms, which no longer redissolves by shaking and allowing to stand three or four minutes, but imparts a turbidity to the deep red solution; HCl must then be added without longer delay, drop by drop, until the fluid, though still dark, becomes clear. After neutralizing in this manner, the amount of acetic acid required to form the desired percentage of the final volume was added, next sodium acetate, and lastly the solution was diluted to the final volume (viz: 300 cc.) before boiling. Long boiling of the precipitate was avoided, one or two minutes sufficing to make the basic acetate settle quickly after removing the heat. The precipitate was washed with

*This acetic acid, by volumetric determination, was found to contain 33.16 p. ct. $C_2H_4O_2$.

nearly boiling water, to which 2 gr. sodium acetate and 1 cc. acetic acid, per litre, had been added, until $AgNO_3$ gave no reaction with the washings.

It may be concluded from the results shown in the table, that by using 4 p. ct. by volume of acetic acid, 1.044 sp. gr., and adhering to the above precautions, a complete separation by one precipitation can be obtained of zinc, and one sufficiently accurate for most purposes of manganese; while the amount of nickel and cobalt that goes down with the iron lessens with increase of acetic acid. The following quantitative separations of iron from zinc and manganese were also made. Precipitation was effected in a volume of 300 cc. containing 12 cc. acetic acid, *i. e.* 4 p. ct. of this volume, and 2 gr. sodium acetate.

Fe taken.	Zn taken.	Mn taken.	Fe found.	Zn found.	Mn found.
.1966 gr.	.1997 gr.	...	.1995 gr.	.1994 gr.	...
.2000 "	.2000 "	...	.1998 "	.1999 "	...
.1996 "	...	.2000 gr.	.1983 "	...	.2002 gr.
.2000 "	...	.2000 "	.1993 "	...	.2001 "

Other Variable Conditions.

A volume less in proportion to the iron present may doubtless be advantageous when large quantities of iron are to be precipitated. The writer, however, would not recommend, on account of increased difficulty of washing, less than 100 cc. per .1 gr. Fe.

Experiments made by E. H. Smith in this laboratory, on the separation of iron from manganese, under exactly the same conditions as described, except that double the amount of sodium acetate was used, gave essentially the same results.

He further ascertained that iron could not be precipitated in presence of a larger amount of acetic acid by increasing the amount of sodium acetate.

Since solutions containing free acid may be neutralized with ammonia or ammonium carbonate instead of sodium carbonate, when the presence of ammonium salts is not objectionable, for example in separating nickel from iron, I have duplicated

some of the above experiments with nickel, with no other change than the addition of ammonium chloride. The results are appended, showing the difference when NH_4Cl is present:

P. ct. by volume of acetic acid (1.044 sp. gr.) added.	P. ct. of Ni in 2d Filtrate.	P. ct. of Ni in 2d Filtrate, when 5 gr. NH_4Cl were added.	Difference.
1	1.770	.904	.866
3	1.468	.708	.760
4	1.219	.511	.708

ON THE ACTION OF IODINE MONOCHLORIDE UPON AROMATIC AMINES.

By A. Michael and Lewis M. Norton.

The action of iodine monochloride on aromatic compounds was first investigated by P. Schuetzenberger* in 1861. He produced mono- and di-iodobenzene by the action of this reagent on sodium benzoate. Soon afterwards, Schuetzenberger and Sengenwald† obtained an iodonitrobenzene by the action of iodine chloride on sodium nitrobenzoate, and they also prepared mono- and di-iodophenol by its action on phenol. Later, Schuetzenberger‡ obtained tri-iodophenol by treating phenol with a large excess of the regeant. In 1864, J. Stenhouse§ investigated the action of iodine monochloride on some aromatic bodies. He obtained tri-iodo-orcin by its action on orcin. Lately,‖ tri-iodoresorcin was made in the same manner from resorcin. Stenhouse, in his research, investigated the behavior of iodine chloride toward the salts of

*Rep. Chim. pure, 3, 145. †Rep. Chim. pure, 4, 144. ‡Bull. Soc. Chim. [2], 4, 102.
§J. Chem. Soc. [2], 2, 327. ‖Ber. d. chem. Gesell. 1876, 1752.

aniline. He obtained a compound from whose proximate analyses he was unable to deduce a satisfactory formula, and he believed that this compound belonged to a new class of organic iodo-compounds. This body will be shown to be identical with tri-iodoaniline, which will be later described.

We have undertaken a new investigation of the action of iodine monochloride upon aromatic amines. It seemed probable that by the action of this compound higher substitution products could be obtained, than by the action of iodine on the amines.

The iodine chloride we employed in this investigation was prepared by passing a stream of dry chlorine over iodine, until the weight of the iodine had increased in the ratio of 1 mol. chlorine to 1 mol. iodine. Iodine chloride, so produced, is a dark red liquid, which solidifies at about 10°; and which can be kept several weeks, without undergoing decomposition, when collected in tightly stoppered bottles.

The reagent was used in the form of vapor. A flask containing the iodine chloride was placed in a hot water bath, and connected with another flask containing a solution of the compound to be acted upon, and a current of dry air passed through the apparatus by means of an aspirator.

Action of Iodine Chloride upon Acetanilide.

The acetanilide was dissolved in a large excess of glacial acetic acid, and iodine chloride passed into the solution in the ratio of 1 mol. ICl to 1 mol. C_8H_9NO. The color of the solution became dark; after standing some hours a copious precipitate, consisting of iodoacetanilide, separated; and the filtrate contained a further quantity, which was precipitated by the addition of water. The iodoacetanilide was thus obtained in the form of a dark colored, crystalline precipitate, and was easily purified by two crystallizations from water. The iodine determination resulted as follows: 0.1588 gr. of substance gave 0.1426 gr. of AgI.

	Calculated for $C_6H_4INH(C_2H_3O)$.	Found.
I	48.65	48.53

When crystallized from water, iodoacetanilide forms white, rhombic plates, whose corners are frequently truncated. It

is slightly soluble in cold, but much more in hot water; alcohol and glacial acetic acid dissolve it very readily. The substance melts at 181½°.

Iodoacetanilide is easily converted by the action of hot, concentrated chlorhydric acid into the chlorhydrate of para-iodoaniline; if this is dissolved in water, and an excess of ammonia added, monoiodoaniline (melting point 60°) is precipitated. The action of iodine chloride upon acetanilide is therefore analogous to that of chlorine or bromine, inasmuch as it furnishes a para-compound.

Para-iodoacetanilide is decomposed by warm concentrated nitric acid, and iodine is set free. A nitro-substitution product of iodoaniline can be obtained by dissolving the iodoacetanilide in a large volume of glacial acetic acid, adding an equal quantity of concentrated nitric acid, and heating a short time on a water bath. By partial neutralization the nitroparaiodoaniline is precipitated as a yellow crystalline mass, and is easily obtained in a pure state by repeated crystallizations from dilute alcohol. The iodine determination was as follows: 0.1639 gr. of substance gave 0.1470 gr. of AgI.

		Calculated for $C_6H_5IN_2O_2$.	Found.
I	...	48.10	48.46

Nitroparaiodoaniline crystallizes from alcohol in long, dark yellow needles, which melt at 122°. It is insoluble in cold and nearly in hot water; easily soluble in alcohol and glacial acetic acid.

There is an important difference between the action of iodine chloride, and that of chlorine or bromine upon acetanilide; these elements form not only mono- but also di- and trichloro- and bromo-substitution products; while by the action of 2 or 3 mols. of ICl upon 1 mol. acetanilide, only the monoiodo-compound is produced. The yield of iodoacetanilide is very satisfactory, reaching 85 per cent. of the amount required by the theory. According to Mills * the yield of iodoaniline by the direct action of iodine on aniline is by no means large, and its production from iodoacetanilide may therefore be recommended.

* Ann. der Chemie, 176, 354.

Action of two Molecules of Iodine Chloride upon one Molecule of Aniline Acetate.

The aniline was dissolved in a large excess of glacial acetic acid, and treated with the calculated amount of iodine chloride, the solution being carefully kept cool during the operation. The liquid became dark colored; and upon the addition of water, a black, partially crystalline mass separated, which was removed by filtration. By repeated crystallizations from alcohol, a nearly pure product was obtained, but it was found to be preferable to treat the black mass at once with steam, in the presence of caustic potash. The compound passes over very slowly, but is subsequently easily purified by a single crystallization from dilute alcohol. The analysis* furnished the following numbers, which correspond to the formula $C_6H_3I_2N$.:

0.2474 gr. of substance gave 0.1940 gr. of CO_2 and 0.0440 gr. of H_2O. 0.1271 gr. of substance gave 0.1719 gr. of AgI. 0.5394 gr. substance gave 19.2 cc. of N. Bar. 776.5; $t = 16°$.

		Calculated for $C_6H_3I_2N$.	Found.
C	...	20.87	21.38
H	...	1.45	1.97
I	...	73.62	73.09
N	...	4.06	4.23
		100.00	

Di-iodoaniline crystallizes in long, white needles, which melt at 95-95½°, and solidify at about 64°. It is almost insoluble in cold water, and but sparingly soluble in hot; in cold alcohol moderately, in hot very easily soluble. It is somewhat soluble in glacial acetic acid and readily in acetic ether. Pure di-iodoaniline is easily carried over by steam, and the slowness with which it passes over in its first purification is due to the presence of foreign substances. Concentrated nitric acid attacks di-iodoaniline in the cold, probably forming a nitro-compound; hot nitric acid decomposes it with the liberation of iodine. Concentrated sulphuric acid blackens it in the cold, and decomposes it upon warming, with the evolution of iodine vapors.

*The iodine determinations in this investigation were made according to the method of Carius. Chromate of lead was employed in the combustions. We have found it impossible to prevent traces of iodine from passing into the absorption apparatus, and for this reason the percentage of hydrogen obtained has usually been too high.

Di-iodoaniline possesses weak basic properties. A solution of di-iodoaniline in hot concentrated chlorhydric acid furnishes upon cooling the chlorhydrate, which separates in long, white needles, whose melting point it was impossible to determine, as they begin to decompose below 100°.

An analysis gave the following numbers: 0.3220 gr. of substance gave 0.1284 gr. of AgCl.

	Calculated for $C_6H_3I_2NHCl$.	Found.
Cl ...	9.33	9.88

The chlorhydrate is easily decomposed by water into the free base and chlorhydric acid.

After the removal of the black mass, from which the di-iodoaniline was obtained, a quantity of white needles separated from the filtrate; these were found to consist of a mixture of mono- and di-iodoaniline. To effect the separation of the two bases, the precipitate was boiled with strong chlorhydric acid; upon cooling, a mixture of the two chlorhydrates separated. This was then treated with water; the chlorhydrate of mono-iodoaniline dissolved, while the salt of di-iodoaniline was decomposed into chlorhydric acid and the base, which remained undissolved. The separation is very complete.

Action of three Molecules of Iodine Chloride upon one Molecule of Aniline Chlorhydrate.

In order to obtain tri-iodoaniline we allowed 3 mols. of iodine chloride to act upon 1 mol. of aniline acetate. Numerous experiments showed that better results could be obtained by substituting a chlorhydric acid solution of aniline, in the place of the aniline acetate. The solution, on treatment with iodine chloride, became dark colored, and a black precipitate soon settled; as soon as the supernatant liquid became clear, this precipitate was removed by filtration. The filtrate was diluted with six times its volume of water, and allowed to stand twelve hours, during which time a mass of reddish colored needles separated. In order to purify this precipitate, it was boiled with a small quantity of glacial acetic acid, by which most of the impurities were removed. For further purification it was dissolved in hot alcohol, boiled twice with

animal charcoal, and then allowed to crystallize. The slightly colored crystals, thus obtained, were finally crystallized five times from alcohol. The analyses of the product, so purified, were as follows: 0.1383 gr. of substance gave 0.2093 gr. of AgI. 0.1092 gr. of substance gave 0.1624 gr. of AgI. 0.4185 gr. of substance gave 0.2398 gr. of CO_2 and 0.0465 gr. of H_2O. 0.6064 gr. of substance gave 12.2 cc. of N. Bar. = 763mm., t = 19°.

	Calculated for $C_6H_4I_3N$.	Found.		Found by Stenhouse. (Mean).
C ...	15.28	15.62		15.66
H ...	.86	1.23		1.07
N ...	2.97	3.08		3.22
I ...	80.89	81.75	80.35	63.23
	100.00			

Tri-iodoaniline crystallizes in long, white needles, which melt at 185½° without decomposition, and solidify at about 146°. It is insoluble in hot and cold water, slightly soluble in concentrated chlorhydric acid and also in cold alcohol. It is tolerably soluble in boiling alcohol; and, when the solution is slowly cooled, it crystallizes in long needles, which bear a striking resemblance to those of sublimed phthalic anhydride. Its best solvents are carbon disulphide and acetic ether, both of which dissolve tri-iodoaniline very readily, and glacial acetic acid, in which it is considerably soluble. It is volatile in a current of steam, but in less degree than the di-iodo-compound. The yield by the method described above is about 15 per cent. of the theoretical amount.

Tri-iodoaniline is not attacked by dilute nitric acid; concentrated acid dissolves it, forming a nitro-compound. Fuming nitric acid decomposes it in the cold, setting free iodine. Its behavior toward sulphuric acid is the same as that of di-iodoaniline. Tri-iodoaniline has no basic properties; it even crystallizes unchanged from concentrated chlorhydric acid.

We have already mentioned that Stenhouse obtained a beautiful crystalline body by the action of iodine monochloride upon aniline salts. The properties of this body coincide with those of tri-iodoaniline, and the analyses made by Stenhouse, whose mean we present, correspond, with the exception of the iodine estimations, well with those we obtained. In

order to remove all doubt, as to the identity of the two bodies, we have repeated the experiments of Stenhouse, and satisfied ourselves that they are identical.

Action of Iodine Chloride on Metanitraniline.

By the direct action of bromine on metanitraniline a tri-bromonitraniline is formed. The analogy between the action of bromine, and that of iodine chloride on aniline led us to expect, that by the action of iodine chloride on metanitraniline, a tri-iodo-compound would be produced; we therefore passed 3 mols. of iodine chloride into a solution of 1 mol. of nitraniline in dilute chlorhydric acid. The solution, thus obtained, was allowed to stand several days, and then diluted with water. A yellow precipitate soon separated. This precipitate contained two compounds, which were separated in the following manner: the precipitate was dissolved in boiling alcohol; on cooling, one of the substances separated in long dark yellow needles, while the other substance remained in solution. The yellow needles were purified by repeated recrystallizations from alcohol, and analyzed with the following results: 0.2083 gr. of substance gave 0.2532 gr. of AgI. 0.4056 gr. of substance gave 0.2826 gr. of CO_2 and 0.0506 gr. of H_2O.

		Calculated for $C_6H_6I_2N_2O_2$.	Found.
C	...	18.46	19.00
H	...	1.02	1.38
I	...	65.12	65.66

Di-iodometanitraniline is almost insoluble in water; alcohol, hot or cold, dissolves it with ease. It is but slightly soluble in cold acetic ether. Its melting point is 145½°. The yield is almost the theoretical amount. Concentrated nitric acid dissolves in the cold without decomposition.

By boiling with concentrated chlorhydric acid, di-iodometanitraniline is converted into its chlorhydrate. This compound crystallizes in white needles, which are very easily decomposed by water. It also decomposes when heated above 50°. An analysis of the salt, dried in a vacuum, gave the following numbers: 0.1372 gr. of substance gave 0.0475 gr. of AgCl.

		Calculated for $C_6H_4I_2N_2O_2HCl$.	Found.
Cl	...	8.30	8.57

The mother-liquors, from which the di-iodometanitraniline was recrystallized, yielded, upon dilution with water, a second iodine compound, together with small quantities of the above described body. This compound crystallizes in yellow plates, and differs from the di-iodometanitraniline, in that it is very soluble in cold acetic ether and much more soluble in alcohol. A partial separation can be effected by means of acetic ether, but we were unable to obtain the compound in a state of purity. It melts between 85 and 95°, and is probably a monoiodometanitraniline. The yield of this compound was not increased by acting upon 1 mol. of nitraniline with 1 mol. of iodine chloride.

Action of Iodine Chloride upon Paranitraniline.

One molecule of nitraniline was dissolved in dilute chlorhydric acid, and treated with 2 mols. of iodine chloride. The liquid was allowed to stand several days, and then diluted with water. A beautiful, yellow, crystalline precipitate gradually separated, which consisted of two compounds. These were separated by extraction with hot water, which dissolved one, while the other remained as a brown crystalline residue. The hot aqueous solution deposited, on cooling, a mass of long, yellow needles, which were easily purified by recrystallization from water. The proximate analysis of the substance, so obtained, gave the following numbers: 0.1559 gr. of substance gave 0.1384 gr. of AgI. 0.3306 gr. of substance gave 0.3360 gr. of CO_2 and 0.0664 gr. of H_2O.

		Calculated for $C_6H_3IN_2O_2$.	Found.
C	...	27.27	27.71
H	...	1.89	2.22
I	...	48.10	47.91

Monc iodoparanitraniline is easily soluble in alcohol and also in hot water, only slightly in cold water. It melts at 105½°. The yield is about 75 p. ct. of the theoretical amount. It is a weak base; the chlorhydric acid salt is very easily decomposed by water, and so unstable that no satisfactory analysis could be obtained.

The brown residue, insoluble in water, mentioned above, consists of a second compound, which was purified by several crystallizations from a mixture of alcohol and nitrobenzene. The yield of this substance was so small that we endeavored to obtain a larger quantity by the action of ClI on the nitraniline, instead of its chlorhydrate. For this purpose 1 mol. of para-nitraniline was dissolved in chloroform, and treated with 2 mols. of iodine chloride. We obtained in this manner the substance in almost the theoretical quantity. Most of the iodine compound separated from the chloroform upon standing; the remainder was obtained by the addition of alcohol, and the evaporation of the chloroform. The body is best purified by two crystallizations from a mixture of equal parts of alcohol and acetic ether. The analysis was as below: 0.1209 gr. of substance gave 0.1460 gr. of AgI. 0.2177 gr. gave 13.5 cc. of N. Bar = 745.5; t = 3°.

		Calculated for $C_6H_4I_2N_2O_2$.	Found.
I	...	65.12	65.25
N	...	7.18	7.50

Di-iodoparanitraniline crystallizes from alcohol in short, bright yellow prisms, which by reflected light have a beautiful blue color. Its melting point is 243½–244°. It is but little soluble in hot alcohol, more in chloroform and acetic ether, very soluble in hot nitrobenzene, from which it crystallizes in plates.

Action of Iodine Chloride upon Paratoluidine.

The ease with which iodine chloride acts upon acetanilide led us to suppose that it would have a like action on acetparatoluide, but we found that it had no action upon it. This result is surprising, since bromine and chlorine both act easily on acettoluide, with the formation of bromine and chlorine substitution products.

We next investigated the action of 1 mol. of iodine chloride upon a solution of 1 mol. of paratoluidine in dilute chlorhydric acid. The liquid was allowed to stand several hours, during which time a black precipitate settled. This was removed by filtration; upon further standing, a flocculent, nearly white precipitate was deposited, which was purified by two crystal-

lizations from dilute alcohol, and the analysis was as follows: 0.1147 gr. of substance gave 0.1516 gr. of AgI.

		Calculated for $C_7H_7I_2N$.	Found.
I	...	70.76	71.47

Di-iodoparatoluidine crystallizes in long, white needles, which often form clusters. It melts at 124½°. It is insoluble in cold water and but slightly soluble in hot, tolerably in cold and easily in hot alcohol. The filtrate from which the iodine compound separated was neutralized with ammonia and yielded unchanged toluidine.

Action of Iodine Chloride upon Paraamidobenzoic Acid.

The acid was dissolved in a large excess of dilute chlorhydric acid, and treated with 2 mols. of iodine chloride. After the treatment the liquid was allowed to stand six hours, and then diluted with a large volume of water. In the course of a day, a white mass, consisting of the iodo derivative of the acid, separated. This was filtered, purified by conversion into the ammonium salt, and decomposition of this salt by chlorhydric acid; this process being repeated several times. The analysis of the substance, thus obtained, was as follows: 0.1588 gr. of substance gave 0.1908 gr. of AgI. 0.3504 gr. of substance gave 0.2820 gr. of CO_2 and 0.0550 gr. of H_2O.

		Calculated for $C_7H_5O_2NI_2$.	Found.
C	...	21.59	21.94
H	...	1.29	1.74
I	...	65.29	64.93

Di-iodopara-amidobenzoic acid crystallizes in white plates, which melt above 300°. In water, alcohol and acetic acid it is insoluble, very slightly soluble in acetic ether. Nitrobenzene dissolves it more readily. The compound does not combine with acids. It is easily soluble in alkalies, forming the corresponding salts. The potassium and ammonium salts crystallize in long, white needles, and are soluble in water. The silver salt was obtained as a flocculent precipitate by the addition of nitrate of silver to an aqueous solution of the ammonium salt. It is slightly soluble in water and alcohol, and very stable toward light. The analysis gave the following result: 0.2917 gr. of substance gave 0.1384 gr. of AgI.

	Calculated for $C_7H_4O_2NI_2Ag$.	Found.
Ag ...	21.99	21.80

The sodium salt is easily obtained, in a state of purity, by dissolving the acid in warm caustic soda; on cooling, the salt separates in long white needles, which are quite insoluble in cold, but tolerably soluble in hot water. The crystals contain 5 mols. of water of crystallization, which they lose by heating at 160°.

The analysis of the salt furnished the following figures: 0.2537 gr. lost at 160° 0.0468 gr. of H_2O.

	Calculated for $C_7H_4NI_2O_2Na+5H_2O$	Found.
H_2O. ...	17.94	18.05

0.2069 gr. of the anhydrous salt gave 0.0316 gr. of NaCl.

Na ...	5.59	6.00

The barium salt was precipitated from an aqueous solution of the ammonium salt by the addition of barium chloride; the product so obtained was purified by two crystallizations from water. The salt is very little soluble in cold water, more soluble in hot, and crystallizes in colorless needles, containing 4 mols. of water of crystallization.

The analysis gave the following figures: 0.4109 gr. lost at 140° 0.0320 gr. of H_2O.

	Calculated for $(C_7H_4I_2NO_2)_2Ba+4H_2O$.	Found.
H_2O ...	7.31	7.78

0.3728 gr. of the anhydrous salt gave 0.0950 gr. of $BaSO_4$.

Ba ...	15.00	14.97

Action of Iodine Chloride upon Meta-amidobenzoic Acid.

The acid was treated, as in the previous case, with 2 mols. of iodine chloride. After standing a few hours, a grey, crystalline mass separated. This product was purified by crystallization, and by conversion into an alkali salt, and decomposition of the salt by chlorhydric acid. The analyses of the substance, so obtained, indicated, that it was a mixture of di- and tri-iodometa-amidobenzoic acids.

Numerous attempts to obtain a separation all failed, owing to the like solubilities of the derivatives and salts of the two acids. The results of the analyses from different preparations were as follows:

	Calculated for $C_7H_5O_2NI_2$.	Calculated for $C_7H_4O_2NI_3$.	Found.			
I ...	65.29	74.41	68.11	67.51	67.33	68.48

The analysis of the silver salt was as follows:

	Calculated for $C_7H_4O_2NI_3Ag$.	Calculated for $C_7H_3O_2NI_2Ag$.	Found.
Ag ...	21.96	17.4	18.96

Iodine chloride does not act upon acetmeta-amidobenzoic acid.

The results obtained in this investigation show the importance of iodine monochloride as a reagent for the production of aromatic iodo-amines.

We present here a tabular view of the cases in which the action of iodine chloride on aromatic compounds has been investigated, showing its substituting power compared with that of bromine and chlorine under similar circumstances. It will be seen that, while iodine chloride replaces hydrogen by iodine in many cases, yet, on the whole, its strength as a substituting agent is less than that of bromine or chlorine.

	Iodine Chloride.	Bromine.	Chlorine.
Acetanilide	mono	mono-di-tri	mono-di-tri
Salts of Aniline	mono-di-tri	mono-di-tri	mono-di-tri
Metanitraniline	di-mono (?)	tri	
Paranitraniline	mono-di	di	di
Acetparatoluide	no action	mono	mono
Salts of Toluidine	di	mono-di	mono-di
Para-amidobenzoic Acid	di	di	
Meta-amidobenzoic Acid	di-tri (?)	tri	
Phenol	mono-tri	mono-di-tri	mono-di-tri
Resorcin	tri	tri-penta	
Orcin	tri	mono-tri-penta	tri-penta

The determination of the position of the iodine atoms in the above described compounds will require a separate re-

search. The weak basic properties of di-iodoaniline, and the absence of basic properties in tri-iodoaniline, indicate that the second and third iodine atoms entering the molecules have taken the ortho position toward the amido group, since among the numerous known di- and trichloro- and bromoanilines, only those, whose halogen atoms are in the ortho position toward the amido group, show a like loss of basic properties.

THE ACTION OF PHTHALIC ANHYDRIDE ON NAPHTHALENE IN THE PRESENCE OF CHLORIDE OF ALUMINIUM.

By Emile Ador and James M. Crafts.

Friedel has shown in a research * made with one of us, that the action of phthalic anhydride on benzene in the presence of chloride of aluminium is expressed by the equation:

$$C_6H_6 + C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}O \quad = \quad C_6H_5 - CO - C_6H_4 - CO - OH.$$

The product, benzoylorthobenzoic acid, is obtained quite pure, and almost in the quantity required by the above equation, when a considerable excess of benzene is taken. If a similar acid could be obtained from naphthalene in equal abundance, the study of its reactions, and particularly of the hydrocarbons to be derived from it, would present considerable interest, and it is from this point of view that we have taken up this subject.

500 gr. naphthalene were heated with 200 gr. pure phthalic anhydride to 100°, and 250 gr. anhydrous chloride of aluminium were gradually added so as to provoke a nearly continuous disengagement of chlorhydric acid. At the end of six hours the product was boiled with water in order to decompose the anhydrous chloride of aluminium. About 50 gr. phthalic acid

* Comptes rendus, 3 Juin, 1878.

were regained by evaporating the aqueous solution. The principal product was a black tarry mass, which was repeatedly digested with a weak solution of caustic soda. This treatment extracted phthalic acid, besides a small quantity of a less soluble acid, which was the body sought. The purification is difficult, and the method which succeeds the best is to bring it to a certain stage of purity by repeated fractional precipitations by an acid from the sodic solution, then to crystallize 8 to 10 times by cooling from a hot solution of benzene or toluene, and finally to crystallize from alcohol until well formed crystals are obtained. Less than 2 gr. of pure acid were thus obtained.

The analysis gave: Subst. = 0.2415 gr.; CO_2 = 0.6890 gr.; H_2O = 0.0980 gr.

		Found.	Calculated for $C_{18}H_{12}O_5$.
C	...	77.85	78.27
H	...	4.51	4.37

The analysis was made after drying the acid at 130°. It appears to contain water of crystallization, but its percentage was not determined. The melting point in a capillary tube was taken of various portions of dried acid, and was always found to be 173.5° (without correction), notwithstanding differences of form according to the mode of crystallization, and the same is true of the first and last portions in a fractional crystallization of the purified acid.

Naphtoylorthobenzoic acid crystallizes from hot absolute alcohol on cooling, in rosettes of microscopic prisms, which appear to have a single terminal face, whose edge is at right angles with the axis of the prism; the mother liquor after cooling deposits single prisms with two oblique terminal faces at either end. From a mixture of equal parts of alcohol and water it crystallizes in little stout prisms like those of phthalic acid.

It is insoluble in water, easily soluble in alcohol, less soluble in cold benzene or toluene; from these latter it crystallizes in indistinct forms. The acid decomposes on distillation.

The barium salt was formed by adding baryta water to an alcoholic solution of the acid and precipitating the excess of baryta by carbonic acid, and crystallizing the salt from its aqueous solution. The analysis of the dried substance gave 20.95 per cent. Ba instead of 19.94, and it is probable that

some basic salt was present, because the solution deposited during the evaporation a crystalline crust which was difficultly soluble in water. We had too little substance to complete the purification or determine the water of crystallization. The crystals dried over sulphuric acid are very hygroscopic, and lose 2.7 per cent. more water on drying at 150° ; at about 160° the salt becomes vitreous, and melts at a higher temperature before decomposing.

The *barium* salt crystallizes by evaporation of the aqueous solution in microscopic needles. It is pretty soluble in water and even in alcohol.

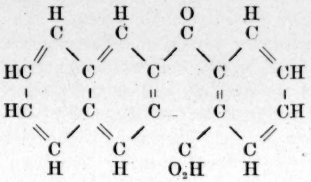
It will be seen by the foregoing statements that the reaction which gives rise to the naphtoylorthobenzoic acid is not a simple one, and that it cannot be prepared in considerable quantity by this method, nor did some other attempts at preparation give more favorable results. It remains to examine the accessory products. The uncrystalline matter which is furnished by the first fractional precipitations of the sodium salt of the acid, as well as the product insoluble in soda after extraction of the naphthalene by boiling alcohol, are very difficult to purify. The latter is the principal product formed in the reaction, and probably contains a certain quantity of naphtoylbenzoic acid. It is a black mass, which is decomposed in great part on distillation at a temperature higher than 300° with formation of a little water. The distillate is a viscous liquid, which, dissolved in benzene, gives on addition of alcohol a small quantity of crystalline flakes. These crystallize from a mixture of ether and alcohol in a granular form. The melting point is 181°–186°. The crystals cannot be sublimed and appear to suffer partial decomposition on distillation. An analysis gave:

		Found.	Pyrene.	Chrysene.
C	...	94.18	94.12	94.73
H	...	5.89	5.88	5.27

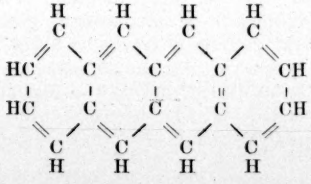
Although the empyrical composition is like that of pyrene or chrysene, the properties of this hydrocarbon are very different. It forms no combination with picric acid, and dilute or concentrated nitric acid does not oxidize it, but gives a resinous nitrated product soluble in alcohol. The solution in bisulphide

of carbon treated with bromine forms a substitution product little soluble in alcohol, easily soluble in ether. It crystallizes in granular form and melts at 112°.

Only one-half gram of the hydrocarbon was obtained, and it must be regarded as an accessory product, so that any theory of its composition which implies its derivation from known bodies by a smooth reaction is entitled to little weight. The following hypothesis, however, may be worthy of notice: From the well-known stability of the hydrocarbon groups entering into the reaction we may suppose the new hydrocarbon to contain the 10 atoms of carbon of naphthalene plus the 8 atoms of phthalic anhydride, and in that case it would be an isomere of chrysene, $C_{18}H_{12}$. It may be derived from naphtoylorthobenzoic acid,



by the closing of the chain and the loss of 3 atoms of oxygen,



This view of the internal structure of the new hydrocarbon is interesting, as it represents it as composed of two molecules of naphthalene having two carbon atoms in common.

GENEVA. *August 1st*, 1879.

NOTE ON PARA-NITRO AND PARA-AMIDO PHENETOL.

By E. J. Hallock.

Phenetol is violently attacked by fuming nitric acid, but is unaffected by concentrated nitric acid in the cold. Cahours, who first tried the action of fuming nitric acid upon phenetol, obtained, he says,* both a solid and liquid product. The former he analyzed and found it to be dinitrophenetol; the latter he supposed to be mononitrophenetol. The writer repeated these experiments with somewhat different results. The dark-red viscous liquid obtained by the action of fuming nitric acid upon pure phenetol, or on a solution of phenetol in acetic acid, was distilled in a current of steam. The product consisted of a solid and a liquid, in varying proportions according to the conditions of the nitration. The solid, when purified by repeated recrystallization both from acid and from alcohol, was proved by an ultimate analysis to be a mononitrophenetol.† Its melting point, 58° C., and other physical properties coincided with that of para-mononitrophenetol, prepared by Fritzsche in 1858 by the action of iodide of ethyl upon the silver salt of paranitrophenol.‡ The writer also obtained the same body by the action of potassium ethylic sulphate and potassic hydrate upon paranitrophenol in sealed tubes at high temperatures. In this operation, however, a considerable quantity of the nitrophenol remained unchanged. Iodide of ethyl and potassic hydrate heated in a sealed tube with paranitrophenetol also yielded, as was expected, the same body, but quite impure. The method of direct nitration yields the purest product, but is quite tedious. When the nitration was performed with nitric acid from which the red fumes had been removed by previously boiling, or by means of hot concentrated acid, the product is mostly liquid

* Ann. Ch. Phys. [3] 27, 461.

† The analysis gave

		Found.	Theory.
C	...	57.3	57.5
H	...	5.9	5.4
N	...	6.0	8.4

‡ Petersb. Acad. Bull. 17, 145; Ann. der Chemie, 110, 155.

and refused to crystallize, even at low temperature. This liquid was apparently a mixture of orthonitrophenetol and unchanged phenetol, holding some paranitrophenetol in solution.

Having obtained a considerable quantity of the paranitrophenetol, an attempt was made to reduce it by means of tin and hydrochloric acid. The resulting salt, after the removal of the tin with sulphydric acid, crystallized from water, in which it was very soluble, in rhombic plates with a pearly lustre. An ultimate analysis* established the composition as $HCl, C_6H_4 \begin{matrix} C_2H_5O \\ NH_2 \end{matrix}$. With platinum chloride it yielded a very beautiful double salt in bright golden flakes, but easily decomposable, especially when heated.

These crystals, when treated with potassic hydrate, yield an oily liquid resembling aniline. It boils at 253° C. (uncorrected), and is doubtless *paramonamidophenetol.* A portion of the salt appears to suffer a farther decomposition, so that the amount of oil obtained was very small. This oil combines, like aniline, directly with acetyl chloride to a crystalline solid. In combination with carbon disulphide it also yields a solid body. The writer did not succeed in obtaining this amidophenetol by the action of ammonic sulphide upon the nitrophenetol at high or low temperature.

The black mass remaining in the flask, after the mononitrophenetol has been distilled off, contains dinitrophenetol, but is difficult to purify.

* The analysis gave

		Found.	Theory.
C	...	55.6	55.4
H	...	7.4	6.9
N	...	8.9	8.1
Cl	...	20.6	20.4

REVIEWS AND REPORTS.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years.

(Continued from page 203.)

Heavy Chemical Manufactures—Acids, Alkalies, and Materials immediately connected therewith.

Sulphur.—By far the largest supplies of native sulphur still come from Sicily, although recent surveys of the volcanic region from whence these supplies are drawn render it improbable that the approach to monopoly which the island has long enjoyed can for many years, say for half a century, be maintained. Of late years the Romagna has added a respectable quota to the Italian supply, and several smaller deposits, as in Galicia, Spain and Egypt, have been worked; but the great field presented in Iceland, of which highly favorable reports have been made, and which has recently, and more than once in the past, been entered upon, has not yet been made practically important. For the future chemical industry of the United States, the deposits at present known which are likely to become of great value are those of Nevada and the adjoining portions of California, the remarkable bed pierced by borings in Western Louisiana but still unworked, and perhaps the volcanic products of Hawaii and the Chilian Andes.

As regards the method of extraction of native sulphur from the gypsum and other earthy materials with which it is found associated, the simple process of piling up the "sulphur stone" in large heaps, arranged very much like those in which charcoal is burned, and melting out part of the sulphur by the heat produced in the smothered combustion of the remainder, is almost exclusively resorted to, and the scarcity of fuel in Southern Italy will probably always cause it to be there retained, in spite of the great loss of sulphur, of which at the best one-third is commonly destroyed or not made available in obtaining the remaining two-thirds. Attempts at less wasteful modes of treatment, as fusion in close vessels by means of high pressure steam, or solution by means of carbon di-sulphide, have made but little progress in the chief regions of production, mainly in consequence of the cost of fuel; the latter process, that by solution, is said to give very satisfactory results in Austrian Galicia. A simple observation made a few

years ago by Sestini,* to the effect that somewhat above 400° C. calcium sulphate and sulphur react upon each other with evolution of sulphur dioxide,

$$CaSO_4 + S_2 = 2SO_2 + CaS,$$

indicates the importance, in the ordinary process, of keeping down the temperature of the heaps of sulphur stone, and this may perhaps serve to diminish the loss in the usual practice. The same precaution is indicated, however, with even greater urgency by recollection of the fact that at a temperature but little above its fusing point melted sulphur begins to thicken, its viscidity soon increasing so much as to greatly impede its draining away from the earthy impurities.

The consumption of sulphur, tending to rapid increase from the ever-growing manufacture of sulphuric acid, the extensive application of late years of sulphur and sulphur compounds to the prevention of grape disease in the vineyards of Europe, and other causes, has been largely economized by the introduction, in workable form and on no small scale, of processes for the artificial making or regeneration of sulphur from the "alkali waste" (calcium sulphide) of the soda manufacture. Of these processes those devised by Mond and Schaffner may be considered typical, both involving partial oxidation of the alkali waste by exposure to air containing carbon dioxide, under regulated conditions of temperature and amounts of air and water, thus producing thio-sulphate and poly-sulphides of calcium, followed by precipitation of sulphur from the mixed solution by hydrochloric acid, calcium chloride being the chief by-product. The final reaction under Mond's treatment seems to be mainly

$$CaS_2O_3 + 2CaS_x + 6HCl = 3CaCl_2 + 3H_2O + S_{2x+2},$$

while Schaffner aims at the result

$$CaS_2O_3 + 2HCl = CaCl_2 + H_2O + SO_2 + S,$$

the SO_2 being passed into fresh alkali waste lye in order to convert more calcium sulphide into thio-sulphate,

$$CaS + SO_2 + O = CaS_2O_3.$$

Other reactions, however, appear to take place to some extent under varying conditions, and it is desirable that in alkali works employing these processes for sulphur regeneration careful account should be kept of the yield actually obtained, and that this should be checked by frequent assays of the material used.

* Bull. de la Soc. Chim. de Paris, 24, (1875), p. 490.

To a very limited, scarcely more than experimental, extent sulphur has also been recovered from the Laming mixture for purifying coal-gas,* essentially ferric hydrate, which, after use in removing sulphur from the gas, may by exposure to the atmosphere be restored to its original condition, with separation of free sulphur, which may be accumulated by repetition of the same steps. Much the greater part, however, of the coal used in making illuminating gas, and practically all that employed as fuel, is so treated as to involve the loss of the whole of the sulphur it contains. For the world at large it is not an excessive estimate to set down this as equal to one per cent. on 270,000,000 tons of coal annually, or 2,700,000 tons — more than seven times the whole sulphur product at present. To this must be added a very large loss from the roasting of sulphurous metallic ores without utilization of the sulphur driven off. The production of sulphur as such from pyrites makes but little progress, and must be viewed as of very secondary importance, but the indirect economy resulting from the large scale on which pyrites is now used for making sulphuric acid is of the greatest value, and has served to prevent scarcity and rise of price of sulphur itself being, before now, sharply felt. The problem of the cheap and practically successful production of sulphur from gypsum remains in abeyance, and seems likely to remain so until the market conditions as to other sources of supply undergo notable change.

No remarkable departure has for some time been made from the established practice of sulphur refining, save that a few years ago the extensive use of flowers of sulphur in combating vine disease led to such regulation of the temperature of the distilling chambers as enabled a larger share than before of the product to be collected in this, the sublimed form.

Acids.

Sulphuric Acid. — The scale upon which this fundamental reagent of the manufacturing chemist is made continues to increase, and there is observable an increasing tendency to connect its production with other industries, so as to secure, when not otherwise attainable, a saving of the heavy charges for transportation of so destructive a material.

It is but forty years since the first decided inducement to substitute pyrites for native sulphur in this manufacture was given by the threatened scarcity of the latter, due to the grant of a monopoly of Sicilian sulphur to a Marseilles house; but within this time, and especially the last few years, the extension of the use of pyrites has been so great that now seven or eight tons of acid are probably made from it for one made from free

* Sulphur from this source is more readily utilized in the manufacture of sulphuric acid.

sulphur. This change has been partly aided by notable improvements in the kilns for burning pyrites, but largely also by the economy effected by metallurgic treatment of the burnt residue. Beginning with the saving of copper from cupriferous pyrites (like that so abundantly found in Spain and Portugal), too poor in this metal to be treated solely as one of its ores, by methods which have already been alluded to in this paper, means have since been found for obtaining also the relatively very minute quantities of silver and gold often found present, and still more recently the burning off of sulphur in the kilns has been so far improved that the residue of ferric oxide may be smelted into pig iron of very fair quality. Beside pyrites, the sulphides of lead, zinc and other metals, and the sulphur of Laming's mixture from coal gas works, have been used, but to a very limited extent only.

As regards the mode of preparing and introducing into the apparatus the nitric acid vapor needed in the production of sulphuric acid, English and Continental practice differ in Europe; in France and Germany, liquid nitric acid, prepared by a separate distillation, is preferred, with a suitable drip contrivance for regulating its flow, while in England "nitre pots" are in general use, heated by the gaseous current from the sulphur or pyrites burners, and adding to this current directly nitric acid vapor. It may seem worth considering whether such addition in the state of vapor might not better be made from small external stills of iron or stoneware, delivering their product into the rear part of the sulphur burner or into the flue leading therefrom, but heated separately, perhaps by steam jacketing of suitable temperature, and thus admitting of independent regulation of temperature.

With a view to determining the best shape and size for the leaden chambers, about which there is still much difference of opinion, it is greatly to be desired that systematic observations, and as far as opportunity may offer experiments, be made upon the scale of actual practice. In the working of the chambers, probably the most valuable novelty has been the introduction by Sprengel, instead of jets of steam, of cold water injected as spray by the aid of a little steam, thus enabling the supply of the necessary amount of water to be combined with the nice regulation of temperature.

Great interest attaches to the comparatively new "Glover tower" which is replacing the old form of de-nitrating tower of Gay Lussac's well-known contrivance for saving nitrous gases. In the original arrangement, the current of gases from the pyrites kilns often required to be cooled before reaching the leaden chambers or the de-nitrating tower, while in the latter the nitrous gases were liberated from the strong acid, brought from the absorbing tower, by means of steam or hot water, thus diluting this acid so far as to unfit it for imme-

diate use again as absorbent. In the upper part of the Glover tower, weak acid from the leaden chambers and strong nitrated acid are allowed to mix, thus liberating the nitrous gases, while in the lower part of the same tower the acid encounters the hot gases from the pyrites kilns, and the transfer of heat from the latter to the former accomplishes the double purpose of cooling suitably the gases and concentrating the acid to such a strength that it can be used over again in the absorbing tower or utilized as part of the final product.

In the transfer of acid from place to place in the works improvements have been effected in the pumps, partly of stoneware capable of resisting the action of the acid, partly bringing to bear compressed air, so that the working parts need not be exposed to contact with the corrosive liquid. Not only in this relation, but in a multitude of chemical processes upon the large scale, the command of hard stoneware, cheap and withstanding well both high temperatures and energetic chemical reagents, is an advantage of the present day comparable with the improved glass and porcelain which our laboratories of research are so well provided with.

The least satisfactory feature of the great manufacture in question is perhaps the amount of nitre still consumed, although this has been much reduced since the days that preceded Gay Lussac's improvements. The chief causes of the loss experienced are doubtless —

1. Gaseous compounds of nitrogen escaping at the final outlet or chimney, where theoretically nothing but atmospheric nitrogen in the free state should find exit, and this in spite of the use of a Gay Lussac's absorbing tower.

2. Nitrous compounds carried off in solution in the liquid acid made, this form of loss probably leading also to increased rate of destruction of the platinum stills for concentration, the metal of which is now known to be slowly but surely dissolved, apparently even by pure sulphuric acid.

3. Reduction of the other oxides or acids of nitrogen to the monoxide or even to elementary nitrogen, both incapable of performing the function of again taking up oxygen from the air. Such reduction, favored by too high a temperature, but liable to occur under conditions not yet, it would seem, fully understood, may take place in the leaden chambers, in the de-nitrating tower, or in the connecting flues back to the nitre pots.

From the careful investigation of this question of nitre consumption, immediately practical results, in the shape of reduced cost of acid production, may be looked for. We are still far from able to make oxygen on a sufficiently great scale, and at a low enough price, to admit of the pure gas being substituted for common air in the chambers, which might in that case be made closed, but it may be well to

avoid laying aside this suggestion, long ago made, as involving a permanently impracticable idea.

For the concentration of the acid to full strength, although glass vessels are not out of use, those of platinum are of most importance, and in the form and arrangement of the latter sundry improvements have been devised, especially by the intelligent firm of Johnson, Matthey & Co. of London. Economy of platinum is secured to a valuable extent by the open pans of the precious metal, with capitals or hoods, connecting tubes, &c., of lead, which have recently been introduced in improved form by Faure and Kessler of Clermont-Ferrand.

In connection with the manufacture of sulphuric acid may be noticed with interest the quite recent production on an industrial scale and presentation in the market of sulphur trioxide or so-called anhydrous sulphuric acid, which replaces with advantage both the ordinary oil of vitriol and the Nordhausen or fuming acid for certain purposes, such as the production of the sulpho-acid-derivatives of benzene, toluene, anthracene, &c., employed in the manufacture of chemical dye-stuffs. The trioxide is obtained by dripping common sulphuric acid into red-hot retorts, thus breaking it up into water, oxygen and sulphur dioxide, condensing the first of these, and causing the two latter to unite by passing them over platinized asbestos or similar porous material at a proper temperature. Both the solid trioxide, retaining but traces of the acid, and an oily, liquid, fuming sulphuric acid, holding 80 or 90 per cent. of trioxide, can now be had at very reasonable prices.

Nitric Acid.—There is little to note with reference to the production of this acid, except that sodium nitrate from Chili may be said to have for some years past become the universally employed material, and horizontal cast-iron cylinders the apparatus generally used for the distillation. Slight modifications in detail of the condensing vessels are made from time to time.

Hydrochloric Acid.—This has long been essentially a secondary product of the alkali manufacture as conducted by the method of Leblanc, but the condensation of the acid has been much improved of late years, the first strong impulse in this direction having been given by the English "Alkali Act" of 1863, directed against the nuisance arising from destruction of vegetation by the acid gas when allowed to escape from the soda works. Since then increased supply of the liquid has conspired with increasing extent and variety of demand for it to still further improve the condensation, and like pains have been bestowed upon the same object in France and Germany. Sandstone or stoneware vessels for the strong acid, and coke towers for the weaker after-products, constitute the apparatus used. A problem already of much importance and promising to become more important in the near future, is presented in

the idea of making, by a cheap and simple process, hydrochloric acid (or chlorine) from the *calcium* and *magnesium* chlorides. The former of these is even now turned out as a waste product of several chemical industries on a very large scale, and from the extension of the ammonia-soda process and other sources vast additional quantities may hereafter be looked for. The latter — magnesium chloride — is available in large amount as a by-product of the treatment of the Stassfurt potash deposits. Solvay's recent proposal to treat these chlorides with silica or alumina can hardly be looked upon as a satisfactory solution of the problem, the temperature required being probably too high for economical results, and the utilization of the solid residues very doubtful.

Acetic Acid.— The two methods by which this acid is made — oxidation of alcohol and destructive distillation of woody fibre — remain without material change, the extent of the manufacture in both directions having, however, grown largely, mainly with the growth of dyeing and calico-printing. The elaborate researches of Pasteur and others upon the phenomena of fermentation have had some little practical application to the work of the vinegar-maker in directing the artificial *sowing* of the ferment organism, and in regulating the conditions for rapid and effectual conversion of the alcohol. The great extension of refined processes of organic chemistry, chiefly among manufacturers of the newer dyes, has produced a demand in the general market for "glacial" acetic acid, which is now made upon a pretty large scale, while but a few years ago it belonged solely to the domain of the scientific and pharmaceutical laboratory.

Oxalic Acid.— Dale's beautiful process for making this product from saw-dust by heating with an alkaline hydrate has displaced all other methods. Founded on experiments of Gay Lussac made half a century ago, the process was first given practically useful shape by Dale in 1856, was for a number of years altogether an English industry, but has of late been adopted also on the Continent of Europe. In Germany caustic potash alone is said to be used, but Dale's own method of working with a mixture of potash and soda (the latter by itself will not answer the purpose) seems distinctly the more advantageous, as allowing of the difficultly soluble sodium oxalate being in large measure purified by washing before it is decomposed by lime. An improvement is said to have been effected by washing the saw-dust beforehand with a weak alkaline solution, thus removing incrusting matter and affording a nearer approach to pure cellulose to be fused with the potassium and sodium hydrates. Great increase of production and lowering of price have followed the successful working of Dale's patent.

Alkalies (Carbonates and Hydrates).

Potash.—Within the last twenty years the production of this alkali has undergone a complete revolution. The crude potash from leaching wood ashes, which formerly represented nearly the whole of the world's supply, has come in much diminished quantity from the forests of Russia, Canada and the Northern United States, and has almost ceased to appear from several of the smaller regions of production—it now forms less than 40 per cent. of the general stock in market. Its place has been largely taken by a purer carbonate made, by Leblanc's classical process, from the sulphate of the newly discovered Stassfurt beds, and by like material derived from the ashes of beet-root molasses, and from the wash water used in cleansing sheep's wool.

In the manufacture of the first of these newer products there have been numerous, and in large measure successful attempts to prepare the sulphate of potassium by crystallizing mixed solutions of the crude potassium chloride (carnallite) and magnesium sulphate (kieserite) found together in the great treasure-house of saline material found overlying the rock salt of the Stassfurt region, but on the whole it seems to have proved more economical to act with sulphuric acid on potassium chloride purified by previous crystallizations and washings, and thus to carry on the whole process as in the common soda manufacture. It is to this method that we must in all probability chiefly look to meet the future increase of demand for potash.

The second method, calcination of the residue from the stills in which the alcohol of beet-root molasses has been driven off, has gained in importance of late years with the rapid increase of production of beet sugar, but the tendency now is, and most likely in the future will be, rather in the opposite direction, more of the crude residues being directly utilized as manure upon the beet crop itself, instead of, as formerly, being worked up into potash for sale. There have been one or two modifications of the method of treatment introduced of late, as the use by Camichel and Henriot of tanner's chestnut extract instead of sulphuric acid to acidify the diluted molasses in preparing it for fermentation, thus obtaining more potassium carbonate and less sulphate after calcination, and the system of C. Vincent of submitting the evaporated still residue to destructive distillation in closed retorts, with a view to utilizing the volatile products (ammonia, trimethylamine, &c.), instead of burning off the organic matter in open hearths.

The third of the newer sources of potash, the "suint" left on evaporation of wash-water from wool factories, has also been employed in both ways, by distillation in retorts, utiliz-

ing the gaseous products for the illumination of the factories (original plan of Maumené and Rogelet), and by calcination in the air. The process seems to have yielded fairly profitable results, but has not established itself on such a scale as to utilize nearly all the washings of even the European wool manufacture. Its general importance is much less than that of the preceding methods.

Soda.—The recent history of the soda manufacture involves notice of improvement in the Leblanc process and of other methods which have been to some extent substituted for it.

1. *Modifications of the Leblanc Process.*— The first step as commonly carried out, decomposition of common salt by sulphuric acid, has been facilitated by the modern use of improved forms of the salt-cake furnace, while no small success has attended the plan proposed by Hargreaves for avoiding the cost of making and using sulphuric acid, by passing a gaseous mixture of sulphur dioxide (from pyrites burners), steam and air through a porous mass of salt heated in a special furnace to a temperature a little below redness. The soundness of the principle on which this method is based was long ago established, and of late the mechanical and other difficulties in detail of application have been so far overcome that salt-cake is regularly made in this way on the large scale by a number of factories in England.

The second stage of the process, fusion of the sodium sulphate with coal and chalk, has been made to profit by two of the prominent features of improved furnace construction, the mechanical "black-ball furnace" being heated by gaseous fuel on the Siemens principle and furnished with a revolving hearth, which enables the hand-working of the contents to be dispensed with and excludes objectionable admission of air. Fuel is economized by the employment of "regenerator" chambers and final use of the waste heat from the escaping gases to evaporate soda liquors from previous operations. At this stage of the chemical treatment Mactear's simple improvement may be noticed, consisting in keeping down the quantity of chalk to the strict demands of theory, and throwing into the hearth, after the reaction is over and just before drawing the charge, a small amount of quick-lime, to be rapidly mixed with the mass by revolving the hearth again for a short time, this last addition serving the purpose, as an excess of calcium carbonate introduced at first had formerly but less advantageously done, of slaking on exposure to moisture, so as to disintegrate the lumps of black-ball and fit them for rapid and effectual leaching.

There has been no recent change of first-rate importance in the process of leaching, nor in the subsequent evaporation of the liquors and purification of the alkali; but the successful utilization of the insoluble residue of the leaching, the "tank

waste," chiefly, as above noticed, for the recovery of sulphur, and to a subordinate extent for the production of sodium thio-sulphate and other purposes for which calcium sulphide may be used, has at the same time reduced the cost of alkali manufacture, and greatly mitigated, if not removed, a long complained of source of nuisance and inconvenience.

2. *Substitutes for the Leblanc Process.*—Of these, in the shape of experiments and patented projects, there have been very many, but only two have established themselves in practical form.

The ammonia-soda process, originally proposed some forty years ago, has but very lately been put into successful working shape by M. Solvay of Brussels. Starting with the same material as that of the Leblanc process, namely common salt, it treats it by an entirely different method, consisting essentially in absorbing gaseous ammonia by strong brine, passing in carbon dioxide under a pressure of about two atmospheres, preventing rise of temperature by special cooling arrangements, and so obtaining a deposit of difficultly soluble acid carbonate of sodium. This is separated, washed and heated to produce the neutral carbonate, while the residual solution, holding ammonium chloride, is heated with lime to drive off ammonia as gas, which is employed in a repetition of the process. The carbon dioxide is obtained by lime-burning with the aid of jets of steam. The intrinsic value of this method and the possibility of its completely replacing that of Leblanc have been much discussed. The latter is still in use for the production of much the larger part of the soda manufactured, while the newer process has proved its capability of at least competing therewith in the markets of the world, and is being extended to new factories, particularly in France.

The chief advantages of the ammonia process may be briefly stated as—

a. Great purity of product.

b. Diminished consumption of fuel.

c. Absence of all noxious escape of gases, either during the manufacture itself or from the waste products.

d. Reduction of loss from, at best imperfectly recovered, valuable material consumed (sulphuric acid of Leblanc process).

e. Possibility of utilizing salt in the form of strong brines, without requiring boiling down to solid salt.

The chief drawbacks of the process are the following:

a. Failure to make the chlorine of the salt available for industrial purposes, this assuming the, at present, useless form of calcium chloride. As has been above noticed, it would be of itself a most important achievement to devise a really workable method of making from this material hydrochloric acid, and hence chlorine and its various derivatives. Such a method would vastly increase the chances of the ammonia process becoming *the* process for the manufacture of soda.

b. Sensible loss of ammonia—although theoretically the same ammonia may be used over and over again indefinitely, and although the loss in practice has been much reduced, it is still not inconsiderable, and hence the process is to a certain extent dependent upon the cost of ammonia, and the effect upon it of varying demand and supply. Improvement in this direction is possible and much to be desired.

c. Imperfect conversion into carbonate of the sodium chloride used. Quite a large part of the salt remains as such mixed with the calcium chloride in the waste residual liquor.

In any discussion of the relative merits of the two systems, the complicated and intricate relations of the by-products to other branches of chemical industry must not be overlooked. In proposing to replace a Leblanc factory by one working the ammonia-soda process, not only has the immediate cost of discarding old "plant" and substituting for it new to be faced, but also the complex and far-reaching commercial disturbance due to breaking up a system of combined manufacture of hydrochloric acid, bleaching powder, chlorate of potash, sulphuric acid, copper saving, &c.

The other partially successful substitute for the Leblanc process, namely the production from cryolite of carbonate of soda, with alum, copperas, &c., as by-products, decomposing the cryolite in the first instance by treatment with lime at a low red heat, leaching the mass with water, precipitating the clear liquor with a stream of carbon dioxide, and evaporating the solution thus freed from aluminum as hydrate, has been worked for some years at Copenhagen, in Denmark, and Natrona, Pennsylvania. It furnishes soda of excellent quality, but the limited supply of cryolite, drawn from a single locality on the ice-bound coast of Greenland, must of itself continue to render the method one of merely subsidiary importance.

A change in the alkali manufacture which should not be left unnoticed is the production no longer of all the soda turned out, or nearly all, in the form of carbonate, a very large amount of the hydrate being now, and for a number of years past, also manufactured, chiefly for soap-boilers' use. Instead, moreover, of rendering caustic the finished carbonate, the crude liquors left after a single crystallization are worked up into caustic soda, which thus becomes an independent product of the factory.

Ammonia.— For several years past there has been large increase of demand not only for ammonium sulphate, but for caustic ammonia, growing out of the extending use of Carré's ice-machines, the advance in refined chemical manufactures, as of organic dye-stuffs, &c., and lately the introduction of the ammonia process for soda manufacture.

The staple, almost the only material used for obtaining ammonia is still gas liquor, and the method of treating it has

not recently undergone any very great change. Direct saturation of the liquor by an acid was long since given up, and distillation of the crude liquor, to which lime is added, usually by means of high-pressure steam, with or without the aid of air blown through the liquid, is practically always resorted to, the ammonia driven out being condensed in acid contained in a separate vessel, and for the most part so manufactured into sulphate; while for the production of caustic ammonia the gas, derived either from decomposition of a previously prepared ammoniacal salt or directly from the crude ammoniacal liquor, is carried into water in condensers presenting adequate surface. There have been a number of improvements in the details of the distilling and condensing apparatus, of which the most noteworthy involve the principle of so-called dephlegmation. A good example may be found in Solvay's recently invented form of apparatus for concentrating the ammoniacal liquor of the gas works.

Dr. Frank has not long since suggested the desirability of saving both the ammonia and the tar, which are at present lost upon a very large scale in the working of coke-ovens; but, while admitting the magnitude of the loss now suffered and the importance of finding means for preventing it, the fact should not be overlooked that in all the processes of destructive distillation carried out on the large scale it has been found very difficult to secure the best results at the same time as to the fixed and the volatile products, preserving meanwhile reasonable economy as to the form of apparatus, simplicity in the method, and amount of labor and time consumed.

The great problem of making ammonia synthetically from atmospheric nitrogen remains apparently as far as ever from an industrially available solution, but numerous attempts at such continue to appear in the form of an annually increasing number of patents.

J. W. MALLET.

REPORT ON PROGRESS IN ANALYTICAL CHEMISTRY.

Hydrogen.—According to J. W. Thomas,* when hydrogen, or any other combustible gas, is mixed with oxygen, and the pressure reduced to 160–170 mm., a complete combustion may be effected by means of the spark, without danger to the eudiometer. The tubes employed may be much shorter than those required when dilution is depended upon to diminish the force of the explosion. To separate hydrogen from marsh gas and nitrogen, W. Hempel† employs with success partially oxidized palladium.

* Jour. Chem. Soc. 1879, 213. † Berichte d. d. chem. Gesellschaft, 12, 636.

From numerous careful experiments on the occlusion of hydrogen by copper, G. S. Johnson* concludes, that it is unsafe to employ the freshly reduced metal in organic analysis, unless it has been previously ignited in a current of nitrogen.

Oxygen.—O. Lindemann† describes an apparatus employed by him for the estimation of free oxygen in the gases of the sulphuric acid chamber by means of wet phosphorus. Mawson and Swan‡ also describe an apparatus for the determination of free oxygen.

G. Huefner§ has published an article on the determination of oxygen and hemoglobine in blood, by means of the spectrophotometric method.

Water.—C. M. Tidy‖ discusses the several methods employed to estimate the organic matter in potable waters. He asserts that the combustion method of Frankland, and the oxidation method by permanganate of potassium, give closely concordant results, while the results of the ammonia process of Wanklyn are often at direct variance with both. He considers the oxidation method more reliable than any other.

G. Lechartier¶ has ascertained that there may be a loss of nitrogen in the Frankland process from both nitrates and ammonium salts during evaporation, the sulphurous acid reducing the former, and the carbonates decomposing the latter. He has furnished new proofs, that when a solution containing salts of ammonium and nitrogenous organic matter is evaporated with magnesia, the ammonia of the former may be completely eliminated without decomposing the latter. He proposes, therefore, to give up the attempt to determine simultaneously the organic carbon and total nitrogen in potable waters; and, instead, to determine 1. the nitrogen remaining after the removal of the ammonia by means of magnesia; 2. the nitrogen contained in the nitrates; 3. the carbon independently.

To determine very minute quantities of carbon in waters and elsewhere, A. Dupré and H. W. Hake** propose two methods. The first consists in conducting the carbonic anhydride obtained by burning the residue in oxygen, into a solution of barium hydroxide, and estimating the precipitated barium as sulphate. The second, called by them nephelometric, consists in conducting the carbonic anhydride into a weak solution of basic acetate of lead, and comparing the turbidity produced with that of standards previously prepared.

Other articles of some interest pertaining to water analysis have appeared under the following titles: "Examination of Water for Bacteria," by C. Himly;†† "On Water Analysis," by E. Bohlig;‡‡ "Investigation of the Mineral Water at Ros-

* Jour. Chem. Soc. 1879, 232.
† Zeitsch. anal. Chemie, 18, 158.
‡ Chem. News, 39, 132.
§ Zeitsch. physiolog. Chemie, 3, 1.
‖ Jour. Chem. Soc. 1879, 46.
¶ Comptes rendus, 89, 231.
** Jour. Chem. Soc. 1879, 159.
†† Zeitsch. anal. Chemie, 18, 117.
‡‡ Zeitsch. anal. Chemie, 18, 195.

heim," by F. B. Power;* "On the Air contained in Sea Water," by H. Tornoë.† H. Geissler‡ has invented and patented an apparatus for the direct determination of water in milk.

Hydrogen Dioxide—E. Schoene§ gives an historical sketch of the several methods employed for the quantitative estimation of hydrogen dioxide, and the results of his own experiments to determine their accuracy. He concludes: 1. That for solutions containing only between .00008 and .001 gr. to the liter his own colorimetric method is the best; 2. that for more concentrated solutions the potassium permanganate volumetric method is accurate; 3. that, next to this, the iodo-acidimetric method of Houzeau is to be recommended; 4. that the gasometric method of Thenard and the iodometric of Brodie are inferior to any of the preceding, both in respect to accuracy and convenience; 5. that it is still uncertain whether indigo can be employed for an exact quantitative estimation of hydrogen dioxide.

Chlorine.—H. Schiff‖ calls attention to and highly commends an old but not widely known method devised by Piria for the analysis of halogen organic compounds. Piria directed that a small platinum crucible containing the substance and filled with black flux be covered by inverting over it another somewhat larger, and the pair then again inverted, the space between them filled with the flux, and heat applied. The method could not be employed for the analysis of compounds containing nitrogen, in consequence of the formation of cyanide of potassium. Schiff, however, fully obviates this difficulty by using a flux consisting of one part of anhydrous sodium carbonate and four or five parts of lime.

To detect or determine chlorine in animal fluids without destruction of the organic matter by combustion, J. Latschenberger and O. Schumann¶ treat a quantity of the fluid with at least an equal volume of a saturated solution of copper sulphate, dilute with water, exactly neutralize with caustic soda, dilute again, filter, and proceed as usual with solutions containing only inorganic matter. This process does not succeed with solutions containing grape-sugar.

Bromine.— H. J. H. Fenton** gives further results of his investigation on the actions of sodium hypochlorite and hypobromite on some nitrogen compounds. Both liberate all the nitrogen of ammonium salts, two-thirds that of guanidine, and one-third that of biuret, while neither decompose the cyanates. The latter liberates all the nitrogen contained in ammonium carbonate and urea, the former only one-half.

W. Foster,†† on the other hand, finds that a solution of alkaline hypobromite liberates only about 92.5 per cent. of

* Jour. prak. Chemie, 19, 223.
† Jour. prak. Chemie, 19, 401.
‡ Dingler's polytech. Jour. 231, 56.
§ Zeitsch. anal. Chemie, 18, 183.
‖ Liebig's Annal. d. Chemie, 195, 293.
¶ Zeitsch. physiolog. Chemie, 3, 161.
** Jour. Chem. Soc. 1879, 12.
†† Jour. Chem. Soc. 1879, 119.

the nitrogen contained in urea: He infers from his experiments that the residual 7.5 per cent. is converted into cyanate.

Iodine.— A. E. Menke* believes that the yellow coloration observed when strong solutions of sulphurous acid and potassium iodide are mixed is due to the formation of iodide of sulphur.

"On the Conduct of concentrated Iodide of Potassium solutions towards Sulphide of Hydrogen," by E. Schering.† See note on page 71 of this Journal, Vol. I.

To separate chlorine, bromine and iodine quantitatively, A. Guyard‡ acidifies the solution containing them with sulphuric acid; adds bisulphite of sodium and sulphate of copper; treats the filtrate from the cuprous iodide, after expulsion of the sulphurous acid, with bichromate of potassium and sulphuric acid; distills the bromine into carbon bisulphide, a solution of sulphurous acid, a sulphite or iodide of potassium, according to the method to be used in its determination; and, finally, precipitates the chlorine as chloride of silver after having reduced the excess of bichromate of potassium by means of a sulphite.

Fluorine.—"On a new Volumetric Method of determining Fluorine," by S. F. Penfield. See this Journal, Vol. 1, p. 27.

"On the Conduct of Silicates containing Fluorine at high Temperatures," by C. Rammelsberg.§

Sulphur.—R. Otto‖ recommends that the sulphide of hydrogen employed to detect arsenic in cases of suspected poisoning, be prepared by treating calcium sulphide with pure hydrochloric acid.

Ad. Carnot¶ directs attention to the fact that Ebelmen long ago advocated the use of sulphide of hydrogen in the dry way in analyses involving the separation of metals whenever a part of the sulphides, which would be thus produced, are volatile and a part non-volatile, or a part soluble in weak acids and a part insoluble. In order to render the method useful for quantitative determinations, the author has undertaken to ascertain which metals give sulphides of constant composition when their compounds are heated in a Rose's crucible in a current of dry sulphide of hydrogen; and finds that manganese, zinc, nickel, silver, lead, bismuth, antimony, tungsten and molybdenum, yield sulphides of constant composition, namely, MnS, ZnS, NiS, AgS, PbS, Bi_2S_3, Sb_2S_3, WS_2 and MoS_2; while iron, cobalt, copper and tin do not.

Ph. de Clermont** gives the results of his experiments on the decomposition of metallic sulphides by salts of ammonium. A boiling solution of chloride of ammonium does not attack the sulphides of bismuth, copper, cadmium, platinum and

* Chem. News, No. 998, 19.
† Ber. d. chem. Gesell., 12, 156.
‡ Bull. de la Soc. Chim. 31, 301.
§ Pogg. Ann. 8, 146.
‖ Ber. d. chem. Gesell. 12, 215.—See note Vol. 1, p. 68 this Journal.
¶ Comptes rendus, 89, 167.
** Bull. d. Soc. Chim. 31, 483.

mercury, but completely decomposes those of antimony and tin, with formation of chloride of antimony, stannic acid, or stannous oxide. It dissolves the sulphides of nickel, cobalt and zinc, somewhat slowly; of iron and manganese, on the other hand, rapidly and completely. Since the hydroxides of aluminum and chromium are insoluble in chloride of ammonium, the author proposes to make use of this reagent to separate them from iron and manganese.

J. Grossmann* determines the amount of sulphurous and hyposulphurous acids in solutions free from sulphates and sulphides, by ascertaining the amount of iodine required for their conversion into sulphate and tetrathionate, and the wt. of sulphate which they yield on complete oxidation. Having obtained these data, the following equations—supposing the acids to be present as sodium salts—enable one to obtain the quantities sought:

$$x + y = \text{A and } \frac{2Na_2SO_4}{I}\,x + \frac{Na_2SO_4}{2I}\,y = \text{B},$$

in which x = I required by $Na_2S_2O_3$, y = I required by Na_2SO_3, A = I required by $Na_2S_2O_3$ and Na_2SO_3, and B = Na_2SO_4 found. If a sulphide is present, it is removed by means of cadmium carbonate. If the solution contains sulphate, it is placed in a flask, treated with $HNaCO_3$, the air displaced by CO_2, HCl added, the SO_2 expelled by heat, and the H_2SO_4 determined as $BaSO_4$ in the filtrate.

A. G. Haddock† recommends the use of a small glass mirror instead of the usual black glass plate in the volumetric estimation of sulphuric acid by means of barium chloride.

B. Delachanal and A. Mermet‡ claim that the method of Fahlberg and Iles § for the determination of sulphur is essentially the same as that formerly described by them.‖

Nitrogen.—W. Hankó: "A new Modification of Simpson's Method of determining Nitrogen."¶

J. Ruffle: "On Total Estimation of Nitrogen by Combustion."**

H. Schiff: "On the Analysis of Organic Compounds containing Nitrogen."††

E. Pflueger: "A new Method of Analysis of Organic Compounds containing Nitrogen."‡‡

A. R. Leeds§§ confirms the statement of F. H. Storer that solutions of ammonium chloride undergo partial nitrification when kept for some months in a dark place.

S. W. Johnson and E. H. Jenkins‖‖: "Determination of Nitrogen, &c."

* Zeitsch. anal. Ch. 18, 79.
† Chem. News, 1011, 156.
‡ Bull. d. Soc. Chim. 32, 50.
§ Ber. d. chem. Gesell. 11, 1187.
‖ Annales de Phys. et de Chim. 12, 88.
¶ Ber. d. chem. Gesell. 12, 451.
** Chem. News, 40, 17.
†† Liebig's Annal. d. Chem. 195, 293.
‡‡ Zeitsch. anal. Chemie, 18, 296.
§§ Chem. News, 39, 17.
‖‖ This Journal, 1, 72.

To determine the total nitrogen in manures containing nitrates by means of Will-Varrentrap's method, A. Rémont* mixes with the material to be analyzed a quantity of powdered white sugar equal in weight to about ten times the nitrates supposed to be present.

R. R. Tatlock† calls attention to the fact that when guano is heated with soda-lime for the purpose of estimating the ammoniacal nitrogen, a part of the nitrates are converted into ammonia in consequence of the presence of organic matter; and hence, that too high results are obtained by adding this nitrogen to that found by a separate determination of the nitrates.

Mawson and Swan‡ give a description of Lunge's nitrometer for the determination of nitrous and nitric acids.

R. Warrington§ publishes the results of the experiments undertaken by him to test the accuracy of the Crum-Frankland method of determining nitric acid as nitric oxide by means of mercury. His conclusions are: 1. That, in the absence of organic matter, the method is one of great accuracy; 2. that the natural error is a small one of deficiency; 3. that the presence of chlorides is no hindrance to its success; 4. that small quantities of organic matter have little or no effect on the result, while large quantities, especially of cane sugar, may cause a considerable deficiency. The presence of chlorides tends to diminish, but does not wholly remove, the error caused by the presence of organic matter.

"On the Titration of Sulphuric and Nitric Acids for Hyponitric Acid," by A. R. Leeds.‖

"On the Detection and Estimation of Nitrous Acid in potable Waters, Acids, &c.," by A. R. Leeds.¶

W. Schroeder** finds that when urine is treated with an acid and quartz or gypsum, and evaporated on the water-bath, the same quantity of nitrogen is obtained from the residue as when the evaporation is conducted under the air-pump, as recommended by C. Voit.†† The author has made some determinations of nitrogen in urine by Seegen's method,‡‡ but his results do not tend towards the establishment of its reliability.

Phosphorus.—According to J. Riban§§ a solution of cuprous chloride in hydrochloric acid may be used with advantage for the determination of phosphide of hydrogen in gaseous mixtures. The product first obtained is a colorless crystalline compound having the formula $Cu_2Cl_2PH_3$, which, however, dissolves on treatment with an excess of the gas.

Some time ago H. Albert and L. Siegfried‖‖ proposed to

* Bull. de Soc. Chim. 31, 242.
† Chem. News, 39, 268.
‡ Chem. News, 39, 183.
§ Jour. Chem. Soc. 1879, 375.
‖ Jour. Americ. Chem. Soc. 1, 18.
¶ Jour. Americ. Chem. Soc. 1, 136.
** Zeit-ch. physiolog Ch. 3, 70.
†† Zeitsch. anal. Ch. 7, 398.
‡‡ Zeitsch. anal. Ch. 3, 155.
§§ Bull. d. Soc. Chim. 31, 385.
‖‖ Zeitsch. anal. Ch. 16, 182.

employ the tartrate of ammonium for separating the reverted phosphoric acid in commercial manures from the insoluble phosphates, instead of the citrate as recommended by Fresenius, Neubauer and Luck. They find, however, on further investigation, that the citrate is to be preferred.* Johnson and Jenkins, on the other hand, state that some experiments of their own, not yet completed, lead them to hope that the tartrate may be successfully substituted for the citrate.† These authors‡ give, also, their mode of procedure to determine phosphoric acid in fertilizers, which consists of separating the phosphoric acid from iron and aluminum by Otto's method, and subsequently determining it by Stolba's.§ The results thus obtained agree very closely with those obtained by the molybdate of ammonium method.

H. Gilbert‖ calls attention to the fact that to determine phosphoric acid volumetrically in the so-called ammonia superphosphates, it is necessary to add a corresponding quantity of ammonium sulphate to the solution of phosphate by which the value of the standard solution of uranium salt is determined.

A. Pavee¶ determines the phosphoric acid in a portion of superphosphate gravimetrically, and then employs the superphosphate itself to ascertain the value of his uranium solution.

Other articles relating to the quantitative determination of phosphorus have appeared under the following titles: "On the Determination of Phosphoric Acid in Fish Guano," by B. E. Dietzell and M. G. Kressner.** "Determination of Silicon and Phosphorus in Iron and Steel," by A. A. Blair.††

Arsenic.—According to W. Johnstone,‡‡ the discovery of the fact that arsenic and antimony can be separated by the action, in their presence, of potassium hydroxide upon aluminum, did not originate with O. Johnson,§§ but with Prof. Filhol.

Under the title of "Critique of the former Method of Bunsen for the Separation of Arsenic from Antimony," L. F. Nilson‖‖ gives a resumé of the facts developed by a previous examination of the method, which tended to show its unreliability;¶¶ and then replies to Bunsen's criticism of his work*** by showing that the separation is imperfect even when the directions of Bunsen are carefully followed.

Antimony and Bismuth.—"Certain characteristic Color-Reactions produced by the Action of Aromatic Hydrocarbons and the Vegetable-Alkaloids on fused Antimony and Bismuth Trichlorides," by W. Smith.†††

Silicon.—"On the Determination of Silicon in Pig Iron and Steel," by T. M. Drown.‡‡‡

* Zeitsch. anal. Ch. 18, 220.
† This Journal, 1, 84.
‡ Ber. d. chem. Gesell. 12, 271.
§ Zeitsch. anal. Ch. 18, 225.
‖ Chem. News, 39, 32.
¶ Zeitsch. anal. Ch. 18, 165.
** Liebig's Ann. d. Ch. 199, 305.
†† This Journal, 1, 86.
‡‡ Zeitsch. anal. Ch. 16, 100.
§§ Zeitsch. anal. Ch. 18, 360.
‖‖ Zeitsch. anal. Ch. 18, 122.
¶¶ Chem. News, 38, 301.
*** Zeitsch. anal. Ch. 16, 417.
††† Chem. News, 70, 26.
‡‡‡ This Journal, 1, 147.

Carbon.—L. Klein* finds that Classen's modification of the Fresenius-Kolbe apparatus† can be employed with advantage for the purpose of determining carbon in pig iron, in the place of that devised by Ullgren.‡

H. N. MORSE.

[*To be continued.*]

THE SUBSECTION OF CHEMISTRY AT SARATOGA.§

On the 27th of August, 1879, the American Association for the Advancement of Science met at Saratoga. Over two hundred and fifty members were in attendance, and of these a far larger proportion than usual were chemists. The subsection of chemistry, therefore, hitherto a decidedly minor feature of the Association, sprang into unwonted prominence, and fairly divided interest with the older and stronger sections, A and B.

In the absence of Professor Remsen, the regular chairman for the year, the subsection re-elected Professor F. W. Clarke of Cincinnati to fill the position thus vacant; and Professor W. R. Nichols of the Massachusetts Institute of Technology was appointed secretary. The manuscript of Professor Remsen's address was, however, received, and was read before the whole of section A by Professor Nichols. It was in substance, briefly, a strong plea for the more thorough study in our country of modern organic chemistry; based partly upon practical and partly upon theoretical considerations.

The real work of the subsection began on Thursday, with a series of papers by Professor A. R. Leeds of Hoboken. The following short notes will give an idea of their character.

"*Action of ozone upon the coloring matter of plants.*"—In this paper Leeds described the exposure of various leaves and colored flowers to ozone. Bleaching took place, as was to be expected; but a considerable percentage of ozone was required to effect it. When such small amounts were employed as are commonly obtained with the phosphorus ozonator, a large volume of air was necessary and a considerable period of time.

"*Bleaching of sugar syrups by ozone.*"—That such bleaching could be effected was not new; but it was shown in this paper that it was readily performed, and that the operation was not attended by any formation of inverted sugar.

"*Reduction of carbonic acid by phosphorus at ordinary temperatures.*"—In certain investigations Professor Leeds found it necessary to ascertain whether or no phosphorus could exert any action upon carbonic acid; a negative result being

* Zeitsch. anal. Ch. 18, 76. † Zeitsch. anal. Ch. 15, 288.
‡ Liebig's Ann. d. Chemie, 124, 59.
§ Communicated at the request of the Editor.

confidently expected. Accordingly, fresh phosphorus was put under water in three ozonators, and the air was then thoroughly expelled by a stream of carbonic acid. The discs upon which the sticks of phosphorus rested were now raised so as to bring the latter in contact with the stream of gas, and abundant reactions for carbonic oxide were speedily obtained. In a second experiment two flasks were filled with carbonic acid, there being at the bottom sticks of phosphorus partly covered by water. Again carbonic oxide was copiously formed. Incidentally to this reaction, phosphuretted hydrogen was produced. In the absence of carbonic acid, this substance did not appear. When water which had been previously boiled to expel air was digested for forty-eight hours with phosphorus at a temperature of 92° to 96°, not a trace of phosphuretted hydrogen could be detected. The reaction with the carbonic acid was probably as follows:

$$6P + 5CO_2 + 3H_2O = P_2O_5 + P_2O_3 + 2PH_3 + 5CO.$$

In immediate connection with this paper Professor Leeds presented a fourth one, entitled "*Oxidation of carbonic oxide by air over phosphorus at ordinary temperatures.*" In this investigation a mixture of air and carbonic oxide was exposed over moist phosphorus. By the action of the nascent ozone carbonic acid was formed.

A fifth paper by Leeds, "*On the solubility of ozone in water,*" was read before the whole of section A on Friday morning. After a critical historical resumé, the reader described experiments to show whether lead plates immersed in aerated and in ozonized water were oxidized differently; whether lead sulphide would be changed into sulphate; and whether silver under like conditions could be peroxidized. Plates of lead, of lead coated with sulphide, and of silver, were immersed in water one centimeter below the surface; and over the surface a stream of thoroughly washed ozonized air was passed. The experiments were varied considerably, but the final results may be concisely summed up thus: The lead was oxidized upon its surface to hydrated monoxide. The lead sulphide was transformed into lead dioxide and free sulphuric acid. The silver was strongly corroded. Hence the ozone, as such, must have been to a certain extent absorbed by the water, beneath which the foregoing substances were attacked. This fact being established, probably Carius' results as to the quantity of ozone soluble in water may be accepted as correct.

Three other papers came before the chemical subsection on Thursday. First, a paper entitled "*Household Chemistry,*" by Mrs. Ellen H. Richards. This was essentially an earnest argument in favor of the study of chemistry by women, and was warmly endorsed by several members in the brief discussion which followed it.

Prof. W. R. Nichols came next in order with a paper, "*On the deterioration of library bindings.*" In a series of analyses of crumbling and decaying leather bindings the author had found unusually large proportions of sulphuric acid; in one instance over eight per cent. This acid he regards as the cause of decay, and, with other chemists, is inclined to attribute its presence to the sulphur in coal gas. The paper, which is to be regarded as a report of progress in the investigation of a much-discussed and still unsettled question, will probably appear in full in the *Library Journal.*

The closing paper on Thursday was by Prof. H. W. Wiley, of Purdue University, on the "*Percentage of sugar in the sap of the sugar maple, and causes which determine its variation; with note on the pressure of sap.*" At the close of the last sugar-making season, which was a poor one, Prof. Wiley began his analyses, using one of the new polariscopes made by Schmidt and Haensch in Berlin. On March 21st, at the beginning of a thaw after a sharp freeze, specimens of sap were taken from twelve trees representing in general the average of the grove. On March 25th, after two days' continuous run, a second series of specimens was taken. The following numbers represent the percentage of sugar in each sample:

		March 21st.	March 25th.
1.	...	3.95	3.44
2.	...	2.95	2.63
3.	...	3.26	2.80
4.	...	2.70	2.34
5.	...	2.70	2.60
6.	...	3.20	2.42
7.	...	2.51	2.00
8.	...	1.95	1.87
9.	...	3.08	2.00
10.	...	2.67	2.34
11.	...	2.70	2.11
12.	...	3.51	2.74

Hence a long-continued flow of sap diminishes the percentage of sugar. A so-called "sweet tree," famous for the quality of its sap, growing on limestone soil in Southern Indiana, gave a sugar percentage of 4.30 at the end of the season. Such "sweet trees" have in general very dark-colored bark. Trees which have been long in use do not yield a sugar as easily crystallizable as that given by younger trees. The investigation is to be continued next spring.

On Friday but three papers were given before the subsection of chemistry. First, "*Observations on the variations in the temperature and chemical character of the water of Fresh Pond, Mass.,*" by W. R. Nichols. This communication was essen-

tially a report of progress, and was not in any way suited for abstraction. It called out, however, considerable discussion, in which pretty nearly the whole ground of variations in water, and water analysis, was gone over. The discussion was mainly a comparison of views rather than an actual argument, and in it Profs. Silliman, Brewer, Leeds, Peckham, Perkins and others took part. A great deal of interest was manifested in the subject, and the members present seemed unanimously to consider the time devoted to it as unusually well spent.

The two other papers of Friday were by Prof. A. A. Breneman of Cornell University. The first of these —"*On the combustion of graphite in analyses of cast iron*"— described certain improvements which could be rendered intelligible only by a diagram or plate, and which were illustrated to the audience both upon the blackboard and by the exhibition of the apparatus itself. The other was entitled "*On colors for salt-glazed pottery.*" In the decoration of such ware the only pigment commonly used is the ordinary cobalt blue. The various tints of brown employed for common stoneware are "slip" colors of fusible clay, and are not salt-glazed, the effect of salt upon them at high temperatures being to cause decoloration by volatilizing the iron as ferric chloride. The tints of pink and green recently shown by Doulton of Lambeth are suited only to the finely decorated pottery known as "Doulton ware." In order to increase the list of colors available for salt-glazed pottery, Prof. Breneman made a series of experiments upon clay tiles in an ordinary stoneware kiln, using all of the common metals capable of coloring fluxes, and also some of the rarer ones like vanadium and molybdenum. Most of his results were simply negative, because of the volatility of the metallic chlorides formed. A few of the results, however, deserve mention. Uranium yellow (sodium uranate), which has long been employed in decorating porcelain, answers admirably for salt-glazed ware if finely powdered before using. It does not fuse, but adheres firmly, takes the glaze, and yields an orange yellow more brilliant than the original color. A mixture of two parts of potassium dichromate, six of borax and one of boric acid, fused and powdered, gives a good brown which takes the glaze perfectly. As borax is apt to "craze" the glazing, the above may be improved by replacing half of that substance by sodium carbonate and omitting the boric acid. Chromic oxide yields better results than the dichromate, and by varying its proportions any shade of brown may be obtained. Solutions of platinic chloride give warm grays, and solutions of gold chloride afford delicate tints of pink. Finely divided gold tends to gather into buttons of metallic appearance. Prof. Breneman exhibited specimen tiles to show the colors produced, and stated his intention of carrying the experiments farther.

Saturday's session of the subsection began with two papers upon gas analysis, entitled as follows: "*A modified method of collecting and measuring gases soluble in water,*" by H. W. Wiley; "*Details of the construction of an apparatus for the analysis of gases,*" by E. W. Morley. As these papers necessarily dealt with experimental details, neither could be rendered intelligible without drawings. They were followed by Mrs. E. A. Smith of Jersey City, who gave an interesting popular account of the great Oberstein industry of cutting, polishing, and artificially coloring agates, and other similar stones. A very beautiful collection of specimens was used to illustrate the paper. After this, a joint communication was presented by W. L. Dudley and F. W. Clarke, describing graphite from the Ducktown copper mine in Tennessee. The mineral mass under discussion was a complex mixture of graphite, copper pyrites, and various silicates. The purest graphite which could be selected from the specimen gave nearly 68 per cent. of carbon, and the ash had approximately the composition of an iron epidote, with the oxygen ratios $RO : 2R_2O_3 : 3SiO_2$. Graphite has never before been reported from this locality. A short note by J. W. Osborne "*On a peculiar case of corrosion of the metal tin,*" came next, followed by the closing paper of the day's session, "*A preliminary notice of a revision of the atomic weights,*" by F. W. Clarke.

The writer, having collected all the published weighings relative to atomic weight determinations, has undertaken their complete recalculation and recombination from the bottom up. He begins with oxygen, for which the atomic weight has been ascertained by the synthesis of water over copper oxide, and by the relative densities of hydrogen and oxygen gases. In the copper oxide method we have nineteen experiments by Dumas, and eight by Erdmann and Marchand. Dumas' results give a mean of 15.9607, with a probable error of $\pm$ .0071. Erdmann and Marchand's mean is 15.9733; $\pm$ .0113. These two means, combined by the usual formula, give a general mean of 15.9642; $\pm$ .006, as the most probable value for the atomic weight of oxygen as ascertained by this method. From the relative densities of oxygen and hydrogen, Regnault's figures, the only series worth considering, give us $O = 15.9628$; $\pm$ .0043. By combining this value with the other, we get a final general mean of $O = 15.9633$; $\pm$ .0035. This value is of course involved in all the subsequent atomic weight calculations, and its probable error affects necessarily all the other probable errors. After oxygen, the elements silver, potassium, sodium, chlorine, bromine, iodine, and sulphur, are discussed in a group. To begin with, all similar data are reduced as far as possible to common standards. For example, there are nine series of determinations of the percentage of oxygen in potassium chlorate. For each series

the mean was calculated, and its probable error; and the nine means were then combined by the ordinary method into one general mean. Thus all the data relative to the seven elements in question were condensed into twenty ratios; and from these, eight independent values for the atomic weight of silver could be deduced. The general mean of these eight values is Ag = 107.675; ± .0096. In this group of elements data were considered from Berzelius, Penny, Pelouze, Marignac, Maumené, Gerhardt, Millon, Struve, Svanberg and Struve, Turner, Dumas, Cooke, and Stas; each series of experiments receiving exactly the weight indicated by the probable error of its mean. The final results were as follows, if O = 15.9633; ± .0035.

Ag = 107.675; ± .0096
Cl = 35.370; ± .0145
Br = 79.768; ± .019
I = 126.557; ± .022
Na = 22.998; ± .011
K = 39.019; ± .012
S = 31.984; ± .012

It is interesting to compare these results with those obtained by Stas alone. Since the latter took for oxygen the atomic weight of sixteen, the figures are comparable only when the new numbers are recalculated by the same standard. We then get the following table:

	New Values.	Stas.	Difference.
Ag ...	107.923	107.930	.007
Cl ...	35.451	35.457	.006
Br ...	79.951	79.952	.001
I ...	126.848	126.850	.002
Na ...	23.051	23.043	.008
K ...	39.109	39.137	.028
S ...	32.058	32.074	.016

These differences, it will be seen, are far within the limits of experimental errors; and the table emphasizes in the most forcible way the magnificent accuracy of Stas' work. No other researches than his could stand so severe a test. At the present date the writer has finished his calculations for forty-three of the elements; and he hopes before long to complete and publish the entire investigation.

On Monday, September 1st, the subsection of chemistry completed its season's work. The session was opened by Professor E. W. Morley, with a striking paper upon "*Results of systematic analyses of air, designed to discover the cause of variations in the quantity of oxygen therein contained.*" This com-

munication, which has appeared in full in the "American Journal of Science and Arts" for September, may be summed up for present purposes very briefly. Professor Loomis has suggested that the so-called "polar waves" may be really sudden vertical descents of cold air from very great elevations. Since oxygen is heavier than nitrogen, it is mathematically probable that air at a great height would be poorer in the former gas than that at ordinary levels. If this be true, and Loomis' theory is correct, then the air which has suddenly fallen upon us during a severe cold snap should contain less oxygen than the average. That this is actually so, and that the variation is far within the limits of experimental error, Prof. Morley has shown; thus confirming in a most curious way the views of Professor Loomis. The investigation is to be carried yet farther, and with additional refinements in the methods of analysis.

Professor W. R. Nichols next gave a brief statement of "*An accidental contamination of a source of water supply.*" This related to a fire near Boston, in which large quantities of sulphuric acid from a burning building flowed into certain bodies of water used to supply parts of the city. The results showed the insignificant effect produced by the contamination.

The next paper, by William McMurtrie of the Agricultural Department at Washington, was only partially chemical, and unfortunately not suited for abstraction. It was entitled "*The limits of meteorological conditions governing the extension of beet root culture*"; and it will appear in full as part of a government report. It was followed by A. A. Breneman, "*On the action of caustic alkaline solutions upon glass.*" In the author's absence, this paper was read only by title. In substance, the communication is as follows: A number of large, green glass bottles were used in the laboratory of Cornell University for holding weak solutions of caustic soda. These bottles were frequently found to be cracked and leaking. Examination showed that minute cracks started from the inner surface of the glass, and slowly developed outward. The explanation suggested is that the thicker portions of the glass were left by imperfect annealing in a state of strain or tension; and that the removal by the caustic soda of small portions of the inner surface disturbed the equilibrium of molecular forces, and led to local rupture.

The closing paper of all was by Professor C. Gilbert Wheeler of Chicago—"*A chemical examination of black ozokerite.*"

The subsection elected as its officers for next year, Prof. J. M. Ordway of Boston, chairman; and Professor C. E. Munroe of the U. S. Naval Academy, secretary. The meeting of the Association will begin in Boston on the last Wednesday of August, 1880; and it is to be hoped that a large number of working chemists may attend, and present for discussion their best material.

PAPERS READ BEFORE SECTION B (CHEMICAL SCIENCE SECTION) OF THE SHEFFIELD MEETING OF THE BRITISH ASSOCIATION.

W. Chandler Roberts.—Report of Committee on the Chemistry of some of the lesser-known Alkaloids.

Walter Weldon.—On some relations between the numbers expressing the Atomic Weights of the Elements.

M. R. D. Silva.—On the Synthesis of Diphenyl-propyl.

F. A. Abel.—Recent Researches in explosive Agents.

Prof. Dewar.—On Vapor Densities.

P. Braham.—To describe a large Crystal of Mercury Sulphate.

Henry S. Bell.—On the Manufacture of Crucible Steel.

Thomas Blair.—On the separation of Iron and Phosphorus, especially with reference to the Manufacture of Steel.

John Hollway.—A New Process in Metallurgy.

A. H. Allen.—A Lecture Experiment in Illustration of the Hollway Process of Smelting Sulphide Ores.

Andrew French.—On Lead Fume, with a description of a New Process of Fume condensing.

Prof. Odling.—On the Constitution of Aluminic Compounds.

A. H. Allen.—On the Presence of Nitrogen in Steel.

A. Vernon Harcourt.—Color tests for Phosphorus and Sulphur in Iron and Steel.

W. Chandler Roberts.—To exhibit some Experiments with Hughes's Voltaic Induction Balance.

J. T. Brown.—Historical sketch of the various Vapor-Density methods.

Prof. Wanklyn.—Note on certain Vapor Densities.

Prof. Wanklyn.—Note on Isocyan-propionic Acid.

G. Ansdell.—Physical constants of Liquid Acetylene and Hydrochloric Acid.

M. de Clermont.—The Action of Ammoniacal Salts of Metallic Sulphides.

W. Ivison Macadam.—On the chemical composition of a Nodule of Ozokerite found at Kinghorn-ness.

Thos. Andrews.—On some curious concretion Balls derived from a Colliery Mineral Water.

Dr. Gilbert.—On some points in connection with Agricultural Chemistry.

T. S. Humpidge.—On the rare Metals of the Yttrium group.

Prof. Dewar.—On the Synthesis of Hydrocyanic Acid.

Prof. Dewar.—On the amount of Nitrous Acid produced in Electric Illumination.

Prof. Dewar.—On the Kinoline Bases.

John M. Thompson.—An account of some recent Experiments on supersaturated Solutions.

J. Norman Lockyer.—Notes of some recent Spectral Observations.

A. H. Allen.—Notes on Petroleum Spirit or Benzoline.

A. Vernon Harcourt.—On the Illuminative Value of a Mixture of Hydrogen.

G. T. Hazelhurst.—On a new Form of Condenser.

W. Thompson.—Notes on a sample of Fuller's Earth found in an old Fullonica recently excavated at Pompeii.

W. H. Watson.—On the Detection of Milk Adulteration.

Dr. Phipson.—Chemical Researches on the *Palmella cruenta.*

Philip Braham.—Description of a glass Burette for collecting, measuring and discharging Gas over Mercury.

CHEMISTRY: GENERAL, MEDICAL, AND PHARMACEUTICAL, INCLUDING THE CHEMISTRY OF THE U. S. PHARMACOPŒIA. A MANUAL OF THE GENERAL PRINCIPLES OF THE SCIENCE, AND THEIR APPLICATIONS IN MEDICINE AND PHARMACY. By John Attfield, M. A. and Ph. D. Eighth edition, revised by the Author. 697 pp. Philadelphia: H. C. Lea.

This work has passed through seven large editions, and appears now for the eighth time within a period of twelve years. In looking for the cause of its popularity, we think it can be found in the fact that, in connection with all the principal chemical substances described, simple, easily followed directions are given, which enable the student to verify every statement by actual experiment. The fundamental idea of the author, and one which he has successfully followed, is expressed in his own words thus: "A good knowledge of chemistry may be acquired synthetically, by preparing considerable quantities of the salts of the different metals, or analytically, by going through a course of pure qualitative analysis. But the former plan demands a larger expenditure of time than most students have to spare, while under the latter system they generally lose sight of the synthetical interest which attaches to analytical reactions. Hence the more useful system, now offered, of studying each metal, etc., from both points of view, time being economized by the operator preparing only small specimens of compounds."

"Chemical synthesis and analysis, thoughtfully and conscientiously followed, will insensibly carry the principles of chemistry into the mind, and fix them there indelibly."

The practice of making small quantities of a large number of representative chemical substances is an excellent one, and should be more general in all laboratories in which chemistry is taught. The tendency to limit instruction to analysis is very extended. When the relations of the six groups into which the elements are usually divided for analytical purposes are mastered, the end is regarded as reached. We cannot but believe that it would be a great gain if much more attention were given to the synthetical side of the subject; and Dr.

Attfield does instructors in chemistry a real service in showing how this result can easily be reached.

While expressing entire approbation of the general principle adopted in the book, we must beg leave to differ from the author when he believes it advisable to select for study, even for medical and pharmaceutical students for whom the book is written, such substances as are of especial importance in medicine and pharmacy. He is right when he says: "The truths of chemistry are the same for all students—crystalline verities which cannot be expanded or compressed to suit any class of workers." These truths are first to be taught, and should be taught by the readiest methods. If, to illustrate a chemical truth, substances which are of especial importance in medicine can just as well be selected, there can be no objection to selecting them. But when substances are selected simply because they are of importance in medicine, and they do not serve the purpose for which they are selected as well as simpler ones which are neglected, then we believe a serious mistake is made. It so happens that a large proportion of pharmaceutical preparations are comparatively complicated chemical substances, the chemistry of which cannot well be understood by the beginner; hence it would be much better to attempt first to teach the general principles of chemistry through substances best adapted to this purpose without any reference to their applications, and then give a subsequent treatise on pharmaceutical substances. Not to go too much into detail, we call attention to the case of lead, pp. 209–215, as illustrating the objectionable method of the author. The salts of this metal described are the acetate, oxyacetate, nitrate, iodide and oleate! It would be difficult to select more awkward examples for a beginner than the oxyacetate and the oleate. In connection with the latter, too, we find a brief description of the action of lead oxide on olive oil.

Another serious objection which may justly be made to the book is, that the subdivision under the heading "Chemistry of Organic Substances" is written without reference to the simplest recognized principles of organic chemistry. The subject is introduced by a description of the alkaloids, a large amount of space being given to the consideration of morphine, quinine, strychnine, &c. The next group of bodies taken up is that containing starch, and the different kinds of sugar. This part of the book could never have been written by one who has a comprehension of the principles of modern organic chemistry, and ought certainly to be entirely rewritten if the book reaches a ninth edition.

While, from what has been said, it is plain that we cannot conscientiously recommend Dr. Attfield's book to the beginner, it is certain that he has brought together a great deal of useful material, and has succeeded in making a very good book of reference for the medical practitioner and the druggist.

BOOKS RECEIVED.

Elements of Modern Chemistry. By Adolph Wurtz. Translated by Wm H. Greene, M. D. Philadelphia: J. B. Lippincott & Co.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the collateral branches. By George Lunge, Ph. D., F. C. S., Professor, &c. London: John Van Voorst.

Supplement to a Handbook of Chemical Manipulation. By C. Greville Williams, F. R. S. London: John Van Voorst.

Experimental Researches in Pure, Applied and Physical Chemistry. By E. Frankland, Ph. D, D. C. L., F. R S. London: John Van Voorst.

Twenty Lessons in Inorganic Chemistry. By W. G. Valentin, F. C. S. New York: G. P. Putnam's Sons.

Jahresbericht ueber die Fortschritte auf dem Gebiete der reinen Chemie. Ludwig Medicus und W. Staedel. Tuebingen: Laupp.

NOTES.

Spectroscopic Investigations.

As previous researches of G. L. CIAMICIAN have shown, chemically related elements have homologous spectra; that is, the individual spectra of the elements of any given group differ from one another only in having their lines displaced towards one end or the other of the spectrum. In the course of a comparative investigation of the spectra of the metals of the alkaline earths, Ciamician has observed phenomena which are adapted to furnishing an explanation of these remarkable relations between the spectra of related elements. When the spectra of the metals of the alkaline earths are produced by allowing the induction spark to pass between the metals (as electrodes) with inserted Leyden jar in an atmosphere of hydrogen, spectra are obtained which show the homology of the lines very beautifully. The spectrum of magnesium, however, can not be compared with the spectra thus obtained, because it does not contain the less refrangible lines. If the jar is removed, or if a weaker battery and a smaller induction

coil is used, all the lines in the red and yellow field in the spectra of calcium and strontium become less intense, and spectra are obtained which are very similar to that of magnesium. If the less refrangible part of the spectrum of the group of the metals of the alkaline earths—that part which is visible only at a high temperature, corresponding to a high electric tension—is compared with the less refrangible half of the complete oxygen spectrum, it is noticed that these two half-spectra exhibit a remarkable similarity (homology). From this it would follow that the spectrum of the group of the metals of the alkaline earths appears to be made up of that of magnesium, and of the less refrangible half of the oxygen spectrum. As it is known that the atomic weights of barium, strontium and calcium can be made up of the atomic weight of magnesium and of oxygen ($24 + 16 = 40$ [calcium], $24 + 4 \times 16 = 88$ [strontium] and $24 + 7 \times 16 = 136$ [barium]), experiments were undertaken to discover whether these remarkable relations in the spectra have any real significance. The author has shown that there exists the same kind of relation between the spectra of carbon and of nitrogen and that of cyanogen, and between the spectra of carbon and of oxygen and the spectrum of carbon monoxide, as that observed between the spectra of magnesium and of oxygen and that of the group of the metals of the alkaline earths. It can hence be said that in all probability the homology of the spectrum lines of chemically related elements depends upon the fact that, in accordance with the regularities in the atomic weights noticed by Mendelejeff, the elements of such natural groups consist of the same components.— (*Wiener Sitzungsberichte*, 79, II. *Abth.*)

Nitrous Oxide as an Anaesthetic.

Paul Bert reports the complete success attending the application of nitrous oxide as an anaesthetic in lengthy surgical operations. A mixture of 85 per cent. of nitrous oxide and 15 per cent. oxygen is administered in the same manner as when used by dentists except that the whole operation takes place in a specially constructed chamber where the pressure of the atmosphere can be varied at the will of the operator. Experience shows the agent to be entirely harmless and to possess many advantages over other anaesthetics in practical use.—(*Comptes rendus*, 89, p. 132.)

On the Conduct of Chlorine at high Temperatures.

In continuing the application of their admirable method for the determination of specific gravities of vapors, Victor and

CARL MEYER have discovered some extremely interesting facts regarding chlorine. They have shown that, while, as is well known, the spec. gr. of chlorine at ordinary temperatures conforms to the law of Avogadro, at a temperature a little above 620° the spec. gr. becomes somewhat less, and then, as the temperature is raised, there is a gradual decrease in the spec. gr. until at about 1200° a minimum is reached. From this point up to 1567° the spec. gr. remains constant and corresponds to the formula $\frac{2}{3}Cl_2$. Hence, according to the authors, *the molecular weight of chlorine, which at low temperatures* (below 600°) *is* 71, *is* 47.3 ($\frac{2}{3}$.71) *above* 1200°. In the course of their remarkable paper the authors use these words: "We postpone for the present any discussion of the theoretical conclusions which are suggested by these experiments and which must lead to a new theory of the halogens." They promise, however, to give special attention to two possible explanations which suggest themselves at once. One of these is founded upon the idea that the quantity of chlorine which has hitherto been considered as the atom is a compound of three atoms of a trivalent element of the atomic weight $\frac{3.5.5}{3}$. The other is the old murium theory so often suggested and as often discarded. In testing this latter theory, it is proposed to allow chlorine heated to 1567° to diffuse through a diaphragm with the object of separating the possibly compound gas into its constituents.—(*Ber. d. chem. Gesell.* 12, 1426.)

Vapor Density of Chlorine.

LIEBEN offers the following suggestions as possible explanations of the change at high temperatures of the vapor density of chlorine:

1. It may be that the coefficient of expansion of chlorine above 700° is somewhat greater than that of oxygen, nitrogen, sulphur and mercury, the other vapors examined by Meyer. It is known that gases at high pressure vary from the law of Mariotte, and vary unequally. The coefficients of expansion of different gases between 1200° and 1600° are unknown, and it is not inconsistent to suppose that the coefficient of chlorine may be greater than that of oxygen, nitrogen, &c., above 700°, while below 700° sensibly equal. If this were the fact, then the vapor density of chlorine referred to air or nitrogen would be less from 1200° to 1600° than from 0° to 600°.

2. It may be that the molecule of chlorine (Cl_2) is dissociated at high temperature, and in a certain interval of temperature there may be an equilibrium such that one-half of the molecules of chlorine are dissociated and the density reduced one-third.—(*Comptes rendus*, 89, 353.)

On Chlor-stannic Acid.

In a bottle containing a pretty strong aqueous solution of stannous chloride which had stood for a year or two, never very tightly closed, J. W. MALLET noticed the formation of a soft solid layer of nearly transparent jellylike material. This was washed and allowed to dry at atmospheric temperature. An analysis showed that the substance contained HCl and SnO_2 in the proportions required by the formula $O=Sn\begin{smallmatrix}Cl\\OH\end{smallmatrix}$, or that of normal stannic acid with one hydroxyl replaced by chlorine, analogous in structure to the chloro-hydrated sulphuric acid of Williamson

$$\begin{matrix}O=\\O=\end{matrix}S\begin{smallmatrix}Cl\\OH\end{smallmatrix}.$$

The change experienced by the original stannous chloride may be supposed to have been

$$SnCl_2 + H_2O + O = HCl + SnO\begin{smallmatrix}Cl\\OH\end{smallmatrix},$$

or else the usual formation of stannous oxychloride and stannic chloride from absorption of oxygen,

$$3SnCl_2 + O = Sn_2Cl_2O + SnCl_4,$$

may have first occurred, followed by the reaction

$$SnCl_4 + 2H_2O = 3HCl + SnO\begin{smallmatrix}Cl\\OH\end{smallmatrix}.$$

The author calls the new substance chlor-stannic acid.—(*Jour. Chem. Soc.* Aug. 1879, 524.)